Regio- and Diastereoselective Synthesis of Diverse Spirocyclic Indenes by Cyclization with Indene-Dienes as Two Carbon Building Blocks

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1. General experimental information

Reactions were monitored by TLC and visualization of the developed chromatogram was performed by ultraviolet light. Unless otherwise noted, all reagents including solvents were obtained from commercial supplier without any purification. The forced-flow column chromatography was performed using silica gel eluting with dichloromethane and petroleum ether. NMR spectra were recorded with tetramethysilane as the internal standard. $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra of CDCl$_3$ or DMSO-d$_6$ solutions were recorded either at 400, 376 and 100 MHz or at 500, 471 and 125 MHz (Bruker Avance), respectively and resonances ($\delta$) are given in parts per million (ppm) relatives to tetramethylsilane (TMS). Data for NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. The X-ray crystal-structure determinations of 3ar, 3ab' and 5aa were obtained on Bruker APEX DUO and Bruker D8 VENTURE PHOTON II systems. All melting points are determined on a SGW X-4 melting apparatus and are uncorrected.

2. Optimization of the reaction conditions of [3+2] cyclization of indene-dienes with N-2,2,2-trifluoroethylisatin ketimines

Table S1. Optimization of the reaction conditions $^a$

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<th>Entry</th>
<th>Cat.</th>
<th>Solvent</th>
<th>T ($^\circ$C)</th>
<th>Cat. Loading (mol%)</th>
<th>Time (days)</th>
<th>Yield (%)</th>
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</table>
22<sup>c</sup> DIPEA  DCM  40  20  5  95

23<sup>d</sup> DIPEA  DCM  40  20  5  84

<sup>a</sup> Reaction conditions: 1<sup>a</sup> (0.2 mmol), 4<sup>a</sup> (0.2 mmol), catalyst (20 mol%), solvent (2.0 mL), 25 °C, 3 days. <sup>b</sup> Yield of isolated 5<sup>aa</sup> after purification by silica gel column chromatography (two isomers). <sup>c</sup> The molar ratios to 1.5:1.0 (1<sup>a</sup>/4<sup>a</sup>). <sup>d</sup> The molar ratios to 2.0:1.0 (1<sup>a</sup>/4<sup>a</sup>).

**3. Optimization of the reaction conditions of catalytic asymmetric [3+2] cyclization of indene-dienes with p-QM.**

**Table S2. Optimization of the reaction conditions**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Additive</th>
<th>Time (h)</th>
<th>dr&lt;sup&gt;b&lt;/sup&gt;</th>
<th>yield&lt;sup&gt;c&lt;/sup&gt; (%)</th>
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<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>24</td>
<td>1:2.8</td>
<td>59</td>
<td>40 (n.d.)</td>
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<tr>
<td>2</td>
<td>B</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>48</td>
<td>1:2</td>
<td>52</td>
<td>38 (n.d.)</td>
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<td>3</td>
<td>A</td>
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<td>N.R.</td>
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<td>4</td>
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<td>120</td>
<td>N.R.</td>
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<td>5</td>
<td>C</td>
<td>-</td>
<td>120</td>
<td>N.R.</td>
<td>-</td>
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</table>
Unless otherwise indicated, the reaction conditions were 1a (0.10 mmol), 2a (0.10 mmol) and additive (20 mol%) in the presence of catalyst (20 mol%) in DCM (1.0 mL) at 25 °C. b the dr was determined by 1H NMR. c Yield of isolated 7aa after purification by silica gel column chromatography (two isomers).

### 4. General experimental procedures for synthesis of compounds 3.

A mixture of Cs$_2$CO$_3$ (0.03 mmol, 0.2 equiv.), 1 (0.15 mmol, 1.0 equiv.) and 2 (0.30 mmol, 2.0 equiv.) and 1,2 - dichloroethane (1.5 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 25 °C for the 24-36 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacu. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 3:1-2:1) to afford pure products 3.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aa)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 78.0 mg, 90% yield (two isomers), 10:1 dr, reaction time = 24 h, m.p. 226.2-227.5 °C. 1H NMR (500 MHz, CDCl_3) δ 8.57 (d, J = 8.2 Hz, 1H), 7.65 (td, J = 7.5, 1.0 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.35 – 7.32 (m, 3H), 7.28 – 7.24 (m, 1H), 7.10 (dd, J = 8.3, 1.2 Hz, 1H), 6.99 (dd, J = 7.7, 1.7 Hz, 1H), 6.92 (td, J = 7.4, 1.2 Hz, 1H), 6.84 (d, J = 2.2 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.09 (s, 1H), 5.29 (s, 1H), 4.03 (d, J = 17.9 Hz, 1H), 3.79 (s, 1H), 3.08 (s, 1H), 1.49 (s, 9H), 1.32 (s, 9H). 13C NMR (125 MHz, CDCl_3) δ 175.1, 154.8, 154.0, 148.6, 136.3, 136.2, 134.9, 134.8, 131.7, 129.7, 129.2, 129.0, 128.9, 128.8, 128.6, 128.4, 126.8, 126.2, 123.9, 121.6, 116.9, 113.9, 112.4, 80.0, 77.4, 77.2, 76.9, 75.3, 59.2, 56.3, 41.3, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 762, 936, 1005, 1151, 1237, 1311, 1441, 1482, 1569, 2220, 2875, 1960, 3033, 3628 cm⁻¹. HRMS (ESI, m/z): calculated for C_{40}H_{38}N_{2}O_{2} [M + H]^+: 579.3006; Found: 597.3001.

**2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-methoxy-2-phenylspiro[chromane-3,2'-inden]-3'(1'H)-ylidene)malononitrile (3ab)**

![Chemical Structure](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.43 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 86.8 mg, 95% yield (two isomers), 6:1 dr, reaction time = 36 h, m.p. 236.5-237.7 °C. 1H NMR (500 MHz, CDCl_3) δ 8.05 (d, J = 2.3 Hz, 1H), 7.33 (q, J = 3.5 Hz, 5H), 7.24 (dt, J = 7.7, 1.9 Hz, 2H), 7.08 (dd, J = 8.3, 1.2 Hz, 1H), 6.98 (dd, J = 7.7, 1.7 Hz, 1H), 6.92 (td, J = 7.4, 1.2 Hz, 1H), 6.84 (d, J = 2.2 Hz, 1H), 6.57 (d, J = 2.2 Hz, 1H), 6.06 (s, 1H), 5.29 (s, 1H), 3.96 (d, J = 17.7 Hz, 1H), 3.90 (s, 3H), 3.78
(s, 1H), 3.00 (d, J = 17.6 Hz, 1H), 1.50 (s, 9H), 1.32 (s, 9H).\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 175.4, 160.0, 154.8, 154.0, 141.3, 137.3, 136.2, 136.1, 134.8, 131.7, 129.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 127.7, 127.4, 124.1, 124.0, 121.6, 117.0, 114.1, 112.4, 108.0, 79.6, 75.3, 60.0, 56.6, 55.8, 40.8, 34.6, 34.3, 30.4, 30.1. IR (KBr) v: 747, 813, 924, 1014, 1114, 1152, 1239, 1304, 1439, 1487, 1559, 1596, 2218, 2875, 2960, 3056, 3610 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{41}\)H\(_{41}\)N\(_2\)O\(_3\) [M + H]\(^+\) 609.3112; Found 609.3112.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-methyl-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ac)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R\(_f\) = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.7 mg, 96% yield (two isomers), 14:1 dr, reaction time = 36 h, m.p. 240.8-241.4 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.38 (s, 1H), 7.49 (dd, J = 7.9, 1.5 Hz, 1H), 7.40 – 7.31 (m, 6H), 7.30 – 7.24 (m, 1H), 7.11 (dd, J = 8.4, 1.2 Hz, 1H), 7.00 (dd, J = 7.7, 1.7 Hz, 1H), 6.93 (td, J = 7.4, 1.2 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 6.60 (d, J = 2.2 Hz, 1H), 6.11 (s, 1H), 5.32 (s, 1H), 4.00 (d, J = 17.8 Hz, 1H), 3.80 (s, 1H), 3.05 (d, J = 17.9 Hz, 1H), 2.52 (s, 3H), 1.52 (s, 9H), 1.35 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 175.2, 154.8, 154.0, 145.9, 138.7, 138.7, 136.5, 136.2, 136.1, 134.8, 131.7, 129.8, 129.2, 128.9, 128.7, 128.4, 126.5, 126.1, 124.0, 121.6, 116.9, 114.0, 112.5, 79.6, 75.3, 59.4, 56.4, 41.0, 34.5, 34.3, 30.4, 30.1, 21.8. IR (KBr) v: 744, 814, 905, 1025, 1145, 1237, 1304, 1439, 1486, 1552, 2218, 2875, 2960, 3056, 3610 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{41}\)H\(_{40}\)N\(_2\)O\(_2\) [M + H]\(^+\) 593.3163; Found 593.3170.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-fluoro-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ac)
indene-1'(3'H)-ylidene)malononitrile (3ad)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.50 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.5 mg, 95% yield (two isomers), 8:1 dr, reaction time = 36 h, m.p. 214.0-215.3 °C. 1H NMR (400 MHz, CDCl_3) δ 8.60 (dd, J = 9.0, 4.9 Hz, 1H), 7.41 - 7.31 (m, 5H), 7.32 - 7.23 (m, 1H), 7.23 (td, J = 8.8, 8.2, 2.0 Hz, 1H), 7.15 (dd, J = 8.0, 2.5 Hz, 1H), 7.11 (dd, J = 8.4, 1.2 Hz, 1H), 7.01 (dd, J = 7.8, 1.7 Hz, 1H), 6.94 (td, J = 7.4, 1.2 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H), 6.57 (d, J = 2.2 Hz, 1H), 6.09 (s, 1H), 5.32 (s, 1H), 4.03 (d, J = 18.2 Hz, 1H), 3.81 (s, 1H), 3.08 (d, J = 18.2 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). 13C NMR (100 MHz, CDCl_3) δ 173.5, 166.8 (d, J = 259.8 Hz), 154.6, 154.1, 151.9 (d, J = 9.9 Hz), 136.3, 136.1, 134.9, 132.5 (d, J = 2.4 Hz), 131.7, 129.6, 129.1 (d, J = 7.2 Hz), 128.8, 128.7, 128.6, 128.6, 128.5, 127.5, 123.6, 121.7, 117.0, 116.8 (d, J = 23.3 Hz), 113.8 (d, J = 22.3 Hz) 112.3, 79.6, 79.5, 75.1, 59.8, 56.3, 41.2, 41.2, 34.5, 34.3, 30.3, 30.3, 30.1. IR (KBr) v: 754, 813, 879, 941, 1000, 1116, 1150, 1168, 1212, 1366, 1441, 1483, 1570, 1599, 2220, 2875, 2958, 3032, 3628 cm⁻¹. HRMS (ESI) m/z: Calcd for C_{40}H_{37}FN_{2}O_{2} [M + H]^+ 597.2912; Found 597.2917.

2-(5'-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ae)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.50 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 89.4 mg, 97% yield (two isomers), 8:1 dr, reaction time = 36 h, m.p. 215.4-216.3 °C. 1H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 8.7 Hz, 1H), 7.51 (dd, J = 8.7, 2.0 Hz, 1H), 7.46 (d, J = 1.9 Hz, 1H), 7.36 (td, J = 7.2, 6.8, 3.8 Hz, 5H), 7.33 – 7.24 (m, 1H), 7.11 (dd, J = 8.4, 1.1 Hz, 1H), 7.01 (dd, J = 7.8, 1.8 Hz, 1H), 6.95 (td, J = 7.4, 1.2 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.09 (s, 1H), 5.33 (s, 1H), 4.02 (d, J = 18.1 Hz, 1H), 3.80 (s, 1H), 3.07 (d, J = 18.2 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). 13C NMR (100 MHz, CDCl₃) δ 173.5, 154.6, 154.1, 150.2, 141.5, 136.3, 136.0, 134.9, 134.7, 131.7, 129.5, 129.3, 129.1, 129.0, 128.8, 128.7, 128.6, 127.5, 127.2, 127.0, 123.5, 121.7, 117.0, 113.7, 112.2, 80.3, 75.1, 59.5, 56.3, 41.0, 34.5, 34.3, 30.3, 30.1. IR (KBr) v: 756, 814, 903, 1001, 1101, 1151, 1235, 1315, 1363, 1440, 1483, 1564, 2221, 2876, 2958, 3030, 3629 cm⁻¹. HRMS (ESI) m/z: Calcd for C₄₀H₃₇ClN₂O₂ [M + H]⁺ 613.2616; Found 613.2614.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3af)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 88.3 mg, 97% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 265.1-266.0 °C. 1H NMR (500 MHz, CDCl₃) δ 8.55 (d, J = 8.1 Hz, 1H), 7.68 (td, J = 7.5, 1.0 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.34-7.31 (m, 1H), 7.27 – 7.20 (m, 1H), 7.08 (dd, J = 8.4, 1.2 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.94 (d, J = 2.2 Hz, 1H), 6.90 (td, J = 7.4, 1.2 Hz, 1H), 6.72 (td, J = 7.5, 1.0 Hz, 1H), 6.68 (dd,
$J = 7.8, 1.8 \text{ Hz, } 1\text{H})$, 6.55 (d, $J = 2.2 \text{ Hz, } 1\text{H}$), 6.36 (s, 1H), 5.26 (s, 1H), 4.19 (d, $J = 18.2 \text{ Hz, } 1\text{H}$), 3.85 (s, 3H), 3.78 (s, 1H), 3.18 (d, $J = 18.3 \text{ Hz, } 1\text{H}$), 1.47 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.2, 159.5, 155.7, 153.9, 148.3, 136.6, 135.9, 134.7, 134.6, 131.8, 130.8, 129.9, 129.1, 129.0, 128.6, 128.2, 127.5, 126.9, 126.1, 124.5, 124.2, 121.3, 119.8, 117.0, 114.0, 112.6, 111.3, 79.9, 70.3, 58.6, 57.3, 56.2, 42.3, 34.5, 34.3, 30.4, 30.1. IR (KBr) v: 759, 938, 1019, 1125, 1153, 1243, 1300, 1373, 1444, 1483, 1570, 1595, 2220, 2873, 2957, 3066, 3617 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{41}$H$_{40}$N$_2$O$_3$ [M + H]$^+$ 609.3112; Found 609.3107.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(o-tolyl)spiro[chromane-3,2'-inden]1'(3'H)-ylidene)malononitrile (3ag)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R$_f$ = 0.45 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 88.3 mg, 99% yield (two isomers), 14:1 dr, reaction time = 24 h, m.p. 243.1-244.3 $^\circ$C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J = 8.1 \text{ Hz, } 1\text{H}$), 7.70 (td, $J = 7.5, 1.1 \text{ Hz, } 1\text{H}$), 7.58 (d, $J = 7.7 \text{ Hz, } 1\text{H}$), 7.54 (d, $J = 7.6 \text{ Hz, } 1\text{H}$), 7.31 (dd, $J = 7.8, 1.4 \text{ Hz, } 1\text{H}$), 7.28 – 7.23 (m, 2H), 7.07 (dd, $J = 8.3, 1.2 \text{ Hz, } 1\text{H}$), 7.00 (dd, $J = 7.8, 1.7 \text{ Hz, } 1\text{H}$), 6.96-6.92 (m, 2H), 6.87 (d, $J = 2.2 \text{ Hz, } 1\text{H}$), 6.60 (d, $J = 7.8 \text{ Hz, } 1\text{H}$), 6.57 (d, $J = 2.1 \text{ Hz, } 1\text{H}$), 6.12 (s, 1H), 5.28 (s, 1H), 4.15 (d, $J = 18.1 \text{ Hz, } 1\text{H}$), 3.81 (s, 1H), 3.18 (d, $J = 18.2 \text{ Hz, } 1\text{H}$), 2.57 (s,3H), 1.48 (s,9H), 1.32 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.7, 155.2, 153.9, 148.2, 140.3, 136.5, 136.0, 134.9, 134.7, 133.4, 132.1, 131.9, 129.9, 129.4, 129.1, 128.8, 128.7, 128.5, 127.1, 126.2, 126.0, 125.4, 124.4, 121.8, 116.8, 113.8, 111.7, 79.8, 73.0, 58.5, 57.1, 42.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) v: 762, 935, 1006, 1126, 1149, 1236, 1302, 1356, 1441, 1478, 1569, 2219, 2870,
2961, 3068, 3610 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{41}\)H\(_{40}\)N\(_{2}\)O\(_2\) [M + H]\(^+\) 593.3163; Found 593.3160.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-ethylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ah)

![Chemical structure of 3ah](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R\(_f\) = 0.37 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 80.0 mg, 88% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 266.4-267.3 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.60 (d, \(J = 8.1\) Hz, 1H), 7.50 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.58 (t, \(J = 7.7\) Hz, 1H), 7.53 (d, \(J = 7.6\) Hz, 1H), 7.39 (d, \(J = 7.3\) Hz, 1H), 7.31 (t, \(J = 7.5\) Hz, 1H), 7.30 – 7.21 (m, 1H), 7.06 (d, \(J = 7.8\) Hz, 1H), 7.00 (dd, \(J = 7.7, 1.4\) Hz, 1H), 7.00 – 6.89 (m, 2H), 6.86 (d, \(J = 2.1\) Hz, 1H), 6.63 – 6.55 (m, 2H), 6.21 (s, 1H), 5.28 (s, 1H), 4.15 (d, \(J = 18.2\) Hz, 1H), 3.81 (s, 1H), 3.18 (d, \(J = 18.3\) Hz, 1H), 3.02-283 (m, 2H), 1.48 (s, 9H), 1.40 (t, \(J = 7.5\) Hz, 3H), 1.32 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 175.5, 155.0, 154.0, 148.3, 145.8, 136.5, 136.0, 134.8, 134.7, 132.8, 131.9, 129.9, 129.9, 129.5, 129.1, 128.8, 128.8, 128.4, 127.1, 126.2, 126.0, 125.1, 124.5, 121.8, 116.8, 113.9, 111.7, 79.9, 72.7, 58.5, 57.0, 42.1, 34.5, 34.3, 30.4, 30.0, 24.9, 14.5. IR (KBr) \(\nu\): 767, 938, 1005, 1125, 1148, 1238, 1302, 1366, 1443, 1480, 1570, 2221, 2872, 2961, 3068, 3613 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{42}\)H\(_{42}\)N\(_{2}\)O\(_2\) [M + H]\(^+\) 607.3319; Found 607.3316.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-fluorophenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ai)

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The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. Rf = 0.23 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 82.9 mg, 93% yield (two isomers), 8:1 dr, reaction time = 36 h, m.p. 223.5-224.1 °C. 1H NMR (500 MHz, CDCl3) δ 8.58 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.36 (q, J = 7.3 Hz, 1H), 7.30 - 7.22 (m, 1H), 7.23 - 7.15 (m, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.99 (d, J = 6.9 Hz, 1H), 6.95 (t, J = 7.4 Hz, 2H), 6.91 (d, J = 2.1 Hz, 1H), 6.76 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 2.1 Hz, 1H), 6.36 (s, 1H), 5.30 (s, 1H), 4.10 (d, J = 18.1 Hz, 1H), 3.81 (s, 1H), 3.19 (d, J = 18.1 Hz, 1H), 1.48 (s, 9H), 1.34 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 174.6, 162.8 (d, J = 246.6 Hz), 154.4, 154.1, 148.5, 138.9, 138.8, 136.3, 136.2, 135.0, 134.9, 131.7, 130.2 (d, J = 8.2 Hz), 129.6, 129.2, 128.8, 128.6, 126.8, 126.3, 124.2 (d, J = 2.8 Hz), 123.8, 121.8, 116.9, 116.2 (d, J = 22.4 Hz). 115.9, 113.8, 112.5, 80.1, 74.6, 59.3, 56.2, 41.0, 34.6, 34.3, 30.4, 30.1. IR (KBr) v: 744, 768, 886, 106, 1169, 1153, 1241, 1313, 1361, 1440, 1482, 1576, 2219, 2874, 2959, 3069, 3630 cm⁻¹. HRMS (ESI) m/z: Calcd for C₄₀H₃₇F₂N₂O₂ [M + H]⁺ 597.2912; Found 597.2916.

2-(2-(2-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aj)

The compound was prepared according to general procedure with petroleum
ether/dichloromethane = 3:1-2:1 as eluent. $R_f = 0.23$ (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.0 mg, 93% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 223.7-224.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J = 8.1$ Hz, 1H), 7.72 (td, $J = 7.5$, 1.1 Hz, 1H), 7.59 (t, $J = 7.7$ Hz, 1H), 7.57 – 7.53 (m, 2H), 7.32 – 7.29 (m, 1H), 7.27 (d, $J = 5.9$ Hz, 1H), 7.11 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.06 (td, $J = 7.7$, 1.3 Hz, 1H), 7.00 (dd, $J = 7.8$, 1.7 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.74 (dd, $J = 8.0$, 1.5 Hz, 1H), 6.57 (d, $J = 2.2$ Hz, 1H), 6.33 (s, 1H), 5.30 (s, 1H), 4.12 (d, $J = 18.2$ Hz, 1H), 3.83 (s, 1H), 3.21 (d, $J = 18.3$ Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.1, 155.2, 154.1, 148.1, 137.9, 136.5, 136.1, 135.1, 134.9, 133.1, 131.9, 131.6, 130.6, 129.8, 129.0, 129.0, 128.6, 127.7, 127.2, 126.3, 126.3, 124.4, 122.0, 117.0, 113.8, 111.4, 80.0, 73.0, 58.6, 57.3, 42.0, 34.6, 34.4, 30.4, 30.2. IR (KBr) v: 749, 904, 939, 1009, 1042, 1161, 1237, 1310, 1322, 1440, 1477, 1572, 2223, 2875, 2959, 3069, 3631 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{40}$H$_{37}$ClN$_2$O$_2$ [M + H]$^+$ 613.2616; Found 613.2614.

2-(2-(2-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ak)

![Structure of 3ak](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. $R_f = 0.26$ (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.5 mg, 87% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 227.3-228.4 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J = 8.1$ Hz, 1H), 7.74 (dd, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.59 (t, $J = 7.7$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 (td, $J = 7.7$, 1.6 Hz, 1H), 7.13 – 7.08 (m, 2H), 7.00 (dd, $J = 7.8$, 1.7 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.72 (dd, $J = 7.9$, 1.5 Hz, 1H), 6.56 (d, $J = 2.2$ Hz, 1H),
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-(trifluoromethyl)phenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3al)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.4 mg, 94% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 220.0-221.1 °C. H NMR (500 MHz, CDCl₃) δ 8.64 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.85 (s, 1H), 6.78 (d, J = 7.9 Hz, 1H), 6.56 (d, J = 5.5 Hz, 2H), 5.30 (s, 1H), 4.01 (d, J = 18.2 Hz, 1H), 3.18 (d, J = 18.2 Hz, 1H), 1.49 (s, 9H), 1.31 (s, 9H). 13C NMR (125 MHz, CDCl₃) δ 175.3, 154.6, 154.1, 148.0, 136.3, 136.1, 135.1, 134.7, 133.9, 131.7, 131.1, 129.7, 129.5, 129.3 (q, J = 5.8 Hz) 129.0, 128.9, 128.8, 128.5, 127.2, 127.1, 126.3, 124.2, 122.0, 117.0, 113.8, 111.6, 79.8, 72.2, 72.2, 58.7, 57.0, 41.6, 34.6, 34.2, 30.3, 29.9. IR (KBr) ν: 763, 931, 1035, 1126, 1236, 1304, 1366, 1440, 1480, 1568, 2221, 657.2111; Found 657.2116.
2875, 1898, 3068, 3632 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{41}$H$_{37}$F$_3$N$_2$O$_2$ [M + H]$^+$ 647.2880; Found 647.2880.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-trifluoromethoxy)phenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3am)

\[
\text{NH}_2\text{CN} \quad \text{OCF}_3 \\
\text{t-Bu} \quad \text{t-Bu} \\
\text{HO} \quad \text{OC}
\]

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R$_f$ = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 79.2 mg, 80% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 258.7-259.5 °C.$^1$H NMR (400 MHz, CDCl$_3$) δ 8.60 (d, $J$ = 8.1 Hz, 1H), 7.72 (t, $J$ = 7.4 Hz, 1H), 7.60 (t, $J$ = 7.7 Hz, 1H), 7.55 (d, $J$ = 7.6 Hz, 1H), 7.42 (d, $J$ = 4.5 Hz, 2H), 7.32 – 7.22 (m, 1H), 7.12 – 7.03 (m, 2H), 7.00 (dd, $J$ = 7.6, 1.4 Hz, 1H), 6.95 (t, $J$ = 7.3 Hz, 1H), 6.90 (d, $J$ = 2.0 Hz, 1H), 6.77 (d, $J$ = 7.8 Hz, 1H), 6.58 (d, $J$ = 2.2 Hz, 1H), 6.36 (s, 1H), 5.31 (s, 1H), 4.11 (d, $J$ = 18.2 Hz, 1H), 3.83 (s, 1H), 3.22 (d, $J$ = 18.2 Hz, 1H), 1.49 (s, 9H), 1.33 (s, 9H).$^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.9, 154.9, 154.0, 149.9, 147.9, 136.3, 136.1, 135.0, 134.8, 131.7, 130.9, 129.6, 128.9, 128.9, 128.5, 127.9, 127.5, 127.1, 126.2, 125.7, 124.1, 121.8, 120.5, 116.8, 113.7, 111.4, 79.9, 70.2, 58.1, 57.0, 41.8, 34.6, 34.2, 30.3, 29.9. IR (KBr) ν: 763, 936, 1009, 1172, 1250, 1301, 1301, 1360, 1444, 1486, 1571, 2221, 2872, 2960, 3071, 3620 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{41}$H$_{37}$F$_3$N$_2$O$_3$ [M + H]$^+$ 663.2829; Found 663.2825.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenoxypyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3an)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R<sub>f</sub> = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.6 mg, 97% yield (two isomers), 9:1 dr, reaction time = 36 h, m.p. 209.6-210.8 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.59 (d, <em>J</em> = 8.1 Hz, 1H), 7.70 (t, <em>J</em> = 7.5 Hz, 1H), 7.58 (t, <em>J</em> = 7.7 Hz, 1H), 7.53 (d, <em>J</em> = 7.6 Hz, 1H), 7.34 (t, <em>J</em> = 7.9 Hz, 2H), 7.32–7.25 (m, 1H), 7.17–7.09 (m, 4H), 6.94 (td, <em>J</em> = 6.5, 5.9, 1.3 Hz, 2H), 6.90 – 6.85 (m, 3H), 6.76 (d, <em>J</em> = 8.2 Hz, 2H), 6.57 (d, <em>J</em> = 2.1 Hz, 1H), 6.49 (s, 1H), 5.26 (s, 1H), 4.16 (d, <em>J</em> = 18.1 Hz, 1H), 3.80 (s, 1H), 3.20 (d, <em>J</em> = 18.1 Hz, 1H), 1.49 (s, 9H), 1.22 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 175.2, 157.6, 157.2, 155.2, 153.9, 148.2, 136.5, 136.0, 134.8, 134.7, 131.6, 130.6, 129.9, 129.6, 129.0, 128.9, 128.7, 128.3, 127.5, 127.0, 126.3, 126.2, 124.3, 123.5, 122.2, 121.5, 119.8, 119.8, 119.0, 116.7, 113.9, 111.5, 79.9, 70.8, 58.4, 57.0, 42.0, 34.6, 34.2, 30.4, 30.3, 29.9. IR (KBr) υ: 747, 863, 1006, 1119, 1156, 1239, 1308, 1372, 1444, 1484, 1575, 2222, 2875, 2958, 3069, 3628 cm<sup>-1</sup>. HRMS (ESI) m/z: Calcd for C<sub>46</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub> [M + H]<sup>+</sup> 671.3268; Found 671.3272.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-methoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ao)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 87.1 mg, 95% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 200.3-201.1 °C. 1H NMR (500 MHz, CDCl_3) δ 8.59 (d, J = 8.2 Hz, 1H), 7.65 (td, J = 7.5, 1.0 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.28 – 7.21 (m, 1H), 7.16 – 7.10 (m, 2H), 7.03 – 6.98 (m, 2H), 6.99 – 6.90 (m, 1H), 6.88 (dd, J = 8.1, 2.3 Hz, 1H), 6.85 (d, J = 2.3 Hz, 1H), 6.59 (d, J = 2.3 Hz, 1H), 6.09 (s, 1H), 5.33 (s, 1H), 4.03 (d, J = 17.9 Hz, 1H), 3.80 (s, 1H), 3.75 (s, 3H), 3.08 (d, J = 17.9 Hz, 1H), 1.51 (s, 9H), 1.34 (s, 9H). 13C NMR (125 MHz, CDCl_3) δ 174.9, 159.6, 154.6, 148.7, 137.8, 136.2, 136.2, 134.9, 134.8, 131.6, 129.7, 129.7, 129.2, 128.8, 128.6, 128.4, 126.7, 126.2, 123.8, 121.6, 120.8, 116.9, 115.1, 114.2, 114.0, 112.5, 80.0, 75.1, 59.4, 56.1, 55.3, 41.2, 34.5, 34.3, 30.3, 30.1. IR (KBr) v: 743, 768, 952, 1014, 1126, 1150, 1239, 1302, 1350, 1441, 1481, 1571, 1722, 2874, 2956, 3072, 3611 cm⁻¹. HRMS (ESI) m/z: Calcd for C_{41}H_{40}N_{2}O_{3} [M + H]^+ 609.3112; Found 609.3115.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(m-tolyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ap)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.34 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 81.7 mg, 92% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 213.2-214.0 °C. 1H NMR (500 MHz, CDCl_3) δ 8.58 (d, J = 8.2 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.29 (s, 1H), 7.30 – 7.23 (m, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H),
7.04 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.84 (s, 1H),
6.56 (s, 1H), 6.06 (s, 1H), 5.30 (s, 1H), 4.03 (d, J = 17.9 Hz, 1H), 3.78 (s, 1H), 3.07 (d, J = 17.9 Hz, 1H), 2.33 (s, 3H), 1.49 (s, 9H), 1.33 (s, 9H). 13C NMR (125 MHz, CDCl₃) δ 175.1, 154.8, 154.0, 148.7, 138.5, 136.3, 136.2, 136.2, 134.8, 131.7, 130.2, 129.8, 129.8, 129.2, 128.8, 128.6, 128.4, 128.4, 128.3, 126.8, 126.2, 125.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.3, 59.3, 56.3, 41.3, 34.5, 34.3, 30.4, 30.1, 21.7. IR (KBr) ν: 739, 768, 903, 1010, 1127, 1147, 1234, 1303, 1356, 1440, 1478, 1556, 2219, 2869, 2690, 3055, 3609 cm⁻¹ cm⁻¹. HRMS (ESI) m/z: Calcd for C₄₁H₄₀N₂O₂ [M + H]^+ 593.3163; Found 593.3171.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-fluorophenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aq)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. Rₛ = 0.31 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 70.3 mg, 79% yield (two isomers), 7:1 dr, reaction time = 36 h, m.p. 215.0-216.1 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.57 (d, J = 8.2 Hz, 1H), 7.65 (td, J = 7.5, 1.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.18-7.14 (m, 1H), 7.12-7.11 (m, 1H), 7.09 (dd, J = 8.4, 1.1 Hz, 1H), 7.04-7.00 (m, 1H), 6.98 (dd, J = 7.7, 1.8 Hz, 1H), 6.93 (td, J = 7.4, 1.2 Hz, 1H), 6.79 (d, J = 2.3 Hz, 1H), 6.55 (d, J = 2.3 Hz, 1H), 6.08 (s, 1H), 5.30 (s, 1H), 3.92 (d, J = 17.9 Hz, 1H), 3.77 (s, 1H), 1.48 (s, 9H), 1.31 (s, 9H). ¹³C NMR (125 MHz, Chloroform-d) δ 174.7, 162.8 (d, J = 246.4 Hz), 154.4, 154.6, 148.5, 138.9, 138.8, 136.4, 136.2, 135.1, 134.9, 131.7, 130.2 (d, J = 8.1 Hz), 129.6, 129.2, 128.8, 128.6, 126.8, 126.3, 124.2 (d, J = 3.2 Hz), 123.8, 121.8, 116.9, 116.2 (d, J = 22.2 Hz). 116.0, 113.8, 112.5, 80.1, 74.6, 59.3,
2-(2-(3-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ar)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. Rf = 0.32 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.9 mg, 94% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 207.2-208.0 °C. 1H NMR (500 MHz, CDCl3) δ 8.58 (d, J = 8.2 Hz, 1H), 7.65 (td, J = 7.5, 0.9 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 6.99 (dd, J = 7.6, 1.4 Hz, 1H), 6.94 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 2.2 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.08 (s, 1H), 5.31 (s, 1H), 3.91 (d, J = 17.8 Hz, 1H), 3.78 (s, 1H), 3.06 (d, J = 17.8 Hz, 1H), 1.49 (s, 9H), 1.32 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 174.6, 154.3, 154.1, 148.5, 138.5, 136.3, 136.1, 135.1, 134.9, 134.8, 131.6, 129.8, 129.5, 129.5, 129.2, 129.2, 128.7, 128.6, 126.8, 126.3, 126.3, 123.7, 121.8, 116.9, 113.8, 112.5, 80.0, 74.5, 59.3, 56.1, 41.0, 34.5, 34.3, 30.4, 30.1. IR (KBr) ν: 747, 766, 872, 1010, 1119, 1153, 1237, 1308, 1361, 1438, 1478, 1569, 2220, 2875, 2959, 3070, 3624 cm⁻¹. HRMS (ESI) m/z: Calcd for C₄₀H₃₇ClN₂O₂ [M + H]⁺ 613.2616; Found 613.2618.

2-(2-(3-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3as)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. $R_f = 0.20$ (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.1 mg, 99% yield (two isomers), 17:1 dr, reaction time = 36 h, m.p. 236.5-237.3 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.59 (d, $J = 8.1$ Hz, 1H), 7.71 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.34 – 7.24 (m, 2H), 7.11 (d, $J = 8.3$ Hz, 1H), 7.06 (td, $J = 7.6$, 1.2 Hz, 1H), 7.00 (dd, $J = 7.8$, 1.6 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.73 (dd, $J = 7.8$, 1.4 Hz, 1H), 6.57 (d, $J = 2.2$ Hz, 1H), 6.33 (s, 1H), 5.30 (s, 1H), 4.12 (d, $J = 18.2$ Hz, 1H), 3.83 (s, 1H), 3.21 (d, $J = 18.2$ Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 175.0, 155.1, 154.0, 148.0, 137.8, 136.4, 136.0, 134.9, 134.8, 133.0, 131.8, 131.5, 130.5, 129.7, 128.9, 128.9, 128.9, 128.5, 127.6, 127.1, 126.2, 126.2, 124.3, 121.9, 116.9, 113.7, 111.3, 79.9, 72.9, 58.5, 57.2, 41.9, 34.5, 34.3, 30.3, 30.1. IR (KBr) ν: 747, 905, 940, 1008, 1042, 1120, 1237, 1301, 1322, 1440, 1478, 1570, 2223, 2875, 2958, 3069, 3632 cm$^{-1}$. HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{40}$H$_{37}$BrN$_2$O$_2$ [M + H]$^+$ 657.2111; Found 657.2116.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3at)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. $R_f = 0.20$ (petroleum ether/ethyl acetate =
20:1). Yellow solid, 78.7 mg, 86% yield (two isomers), 10:1 dr, reaction time = 36 h, m.p. 211.6-212.7 °C. 1H NMR (500 MHz, CDCl$_3$) δ 8.56 (d, $J = 8.1$ Hz, 1H), 7.65 (td, $J = 7.5$, 1.0 Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.30 – 7.21 (m, 3H), 7.08 (dd, $J = 8.4$, 1.2 Hz, 1H), 6.98 (dd, $J = 7.8$, 1.7 Hz, 1H), 6.91 (td, $J = 7.4$, 1.2 Hz, 1H), 6.88 – 6.81 (m, 3H), 6.55 (d, $J = 2.2$ Hz, 1H), 6.01 (s, 1H), 5.29 (s, 1H), 4.04 (d, $J = 17.9$ Hz, 1H), 3.77 (s, 4H), 3.07 (d, $J = 18.0$ Hz, 1H), 1.48 (s, 9H), 1.32 (s, 9H). 13C NMR (125 MHz, CDCl$_3$) δ 175.2, 159.8, 154.9, 154.0, 148.6, 136.4, 136.2, 134.9, 134.8, 131.7, 130.3, 129.8, 129.2, 128.8, 128.6, 128.4, 128.2, 126.8, 126.2, 123.9, 121.5, 117.0, 114.1, 114.0, 112.4, 80.0, 75.0, 59.4, 56.5, 55.4, 41.4, 34.5, 34.3, 30.4, 30.1. IR (KBr) ν: 730, 763, 914, 1001, 1030, 1176, 1234, 1306, 1361, 1442, 1473, 1570, 1610, 2222, 2876, 2960, 3069, 3628 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{41}$H$_{40}$N$_2$O$_3$ [M + H]$^+$ 609.3112; Found 609.3115.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(p-tolyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3au)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. $R_f = 0.35$ (petroleum ether/ethyl acetate = 20:1). Yellow solid, 84.6 mg, 95% yield (two isomers), 10:1 dr, reaction time = 36 h, m.p. 220.8-221.7 °C. 1H NMR (500 MHz, CDCl$_3$) δ 8.58 (d, $J = 8.1$ Hz, 1H), 7.66 (td, $J = 7.5$, 1.0 Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.26 (d, $J = 2.9$ Hz, 2H), 7.24 (d, $J = 2.3$ Hz, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 1H), 6.99 (dd, $J = 7.8$, 1.7 Hz, 1H), 6.93 (td, $J = 7.4$, 1.2 Hz, 1H), 6.85 (d, $J = 2.3$ Hz, 1H), 6.57 (d, $J = 2.2$ Hz, 1H), 6.06 (s, 1H), 5.30 (s, 1H), 4.06 (d, $J = 17.9$ Hz, 1H), 3.79 (s, 1H), 3.08 (d, $J = 18.0$ Hz, 1H), 2.33 (s, 3H), 1.50 (s, 9H), 1.33 (s, 9H). 13C NMR (125
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-ethylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3av)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. Rf = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 83.6 mg, 92% yield (two isomers), 13:1 dr, reaction time = 36 h, m.p. 222.8-223.5 °C. 

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.58 (d, $J_{1} = 8.2$ Hz, 1H), 7.66 (td, $J_{2} = 7.5, 1.0$ Hz, 1H), 7.57 – 7.50 (m, 1H), 7.48 (d, $J_{3} = 7.7$ Hz, 1H), 7.30 – 7.22 (m, 3H), 7.16 (d, $J_{4} = 8.2$ Hz, 2H), 7.13 – 7.07 (m, 1H), 6.99 (dd, $J_{5} = 7.7, 1.4$ Hz, 1H), 6.96 – 6.89 (m, 1H), 6.85 (d, $J_{6} = 2.1$ Hz, 1H), 6.57 (d, $J_{7} = 2.2$ Hz, 1H), 6.07 (s, 1H), 5.30 (s, 1H), 4.06 (d, $J_{8} = 17.9$ Hz, 1H), 3.79 (s, 1H), 3.08 (d, $J_{9} = 17.9$ Hz, 1H), 2.63 (q, $J_{10} = 7.7$ Hz, 2H), 1.50 (s, 9H), 1.33 (s, 9H), 1.22 (t, $J_{11} = 7.6$ Hz, 3H). 

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 175.2, 154.9, 154.0, 148.6, 145.0, 136.4, 136.2, 134.8, 134.8, 133.4, 131.7, 129.8, 129.2, 128.9, 128.8, 128.6, 128.4, 128.3, 128.2, 126.8, 126.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.2, 59.3, 56.4, 41.4, 34.5, 34.3, 30.4, 30.1, 28.6, 15.3. IR (KBr) v: 762, 927, 1012, 1125, 1155, 1234, 1309, 1362, 1440, 1477, 1566, 2222, 2960, 3611 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{42}$H$_{40}$N$_2$O$_2$ [M + H]$^+$ 607.3319; Found 607.3320.
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.50 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.0 mg, 98% yield (two isomers), 14:1 dr, reaction time = 36 h, m.p. 242.5-243.1 °C.\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.58 (d, \(J\) = 8.2 Hz, 1H), 7.65 (td, \(J\) = 7.5, 1.0 Hz, 1H), 7.53 (t, \(J\) = 7.7 Hz, 1H), 7.48 (d, \(J\) = 7.8 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.18 (d, \(J\) = 8.3 Hz, 2H), 7.09 (d, \(J\) = 7.8 Hz, 1H), 6.98 (dd, \(J\) = 7.7, 1.7 Hz, 1H), 6.92 (td, \(J\) = 7.4, 1.2 Hz, 1H), 6.84 (d, \(J\) = 2.3 Hz, 1H), 6.56 (d, \(J\) = 2.3 Hz, 1H), 6.07 (s, 1H), 5.29 (s, 1H), 4.05 (d, \(J\) = 17.9 Hz, 1H), 3.78 (s, 1H), 3.08 (d, \(J\) = 18.0 Hz, 1H), 2.93-2.83 (m, 1H), 1.49 (s, 9H), 1.33 (s, 9H), 1.23 (s, 3H), 1.21 (s, 3H).\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 175.3, 154.8, 154.0, 149.6, 148.7, 136.4, 136.2, 134.8, 134.8, 133.4, 131.7, 129.8, 129.2, 128.8, 128.8, 128.6, 128.4, 126.9, 126.8, 126.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.2, 59.3, 56.4, 41.4, 34.5, 34.3, 33.9, 30.4, 30.1, 23.9, 23.9. IR (KBr) \(\nu\): 732, 839, 920, 1005, 1149, 1233, 1302, 1355, 1440, 1473, 1568, 2221, 2872, 2959, 3065, 3604 cm\textsuperscript{-1}. HRMS (ESI) m/z: Calcd for C\textsubscript{43}H\textsubscript{44}N\textsubscript{2}O\textsubscript{2} [M + H]\textsuperscript{+} 621.3476; Found 621.3479.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ax)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R$_f$ = 0.30 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 82.9 mg, 93% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 225.8-226.3 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J = 8.2$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.24 (m, 1H), 7.10 (dd, $J = 8.3$, 1.1 Hz, 1H), 7.07 – 6.98 (m, 3H), 6.94 (td, $J = 7.4$, 1.2 Hz, 1H), 6.84 (d, $J = 2.2$ Hz, 1H), 6.57 (d, $J = 2.2$ Hz, 1H), 6.08 (s, 1H), 5.32 (s, 1H), 4.00 (d, $J = 18.0$ Hz, 1H), 3.81 (s, 1H), 3.10 (d, $J = 18.0$ Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 174.9, 162.8 (d, $J = 248.9$ Hz), 154.6, 154.1, 148.4, 136.3, 136.2, 135.0, 134.9, 132.2 (d, $J = 3.3$ Hz), 131.7, 130.8 (d, $J = 8.3$ Hz), 129.6, 129.2, 128.7, 128.5, 126.8, 126.3, 123.8, 121.7, 116.9, 115.8 (d, $J = 21.6$ Hz), 113.8, 112.5, 80.0, 74.7, 59.3, 56.3, 41.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) $\nu$: 744, 785, 936, 1008, 1154, 1235, 1309, 1360, 1441, 1479, 1563, 2220, 2875, 2959, 3070, 3627 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{40}$H$_{37}$FN$_2$O$_2$ [M + H]$^+$ 597.2912; Found 597.2913.

2-(2-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ay)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. \( R_f = 0.35 \) (petroleum ether/ethyl acetate = 20:1). Yellow solid, 80.7 mg, 91% yield (two isomers), 16:1 dr, reaction time = 36 h, m.p. 223.7-224.5 °C.\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.57 (dd, \( J = 8.2, 2.8 \) Hz, 1H), 7.65 (dt, \( J = 7.5, 3.7 \) Hz, 1H), 7.53 (t, \( J = 6.8 \) Hz, 1H), 7.47 (d, \( J = 6.7 \) Hz, 1H), 7.31 (t, \( J = 2.4 \) Hz, 4H), 7.26 (d, \( J = 3.0 \) Hz, 1H), 7.11 – 7.05 (m, 1H), 6.99 (d, \( J = 7.6 \) Hz, 1H), 6.97 – 6.89 (m, 1H), 6.81 (s, 1H), 6.55 (s, 1H), 6.06 (d, \( J = 2.9 \) Hz, 1H), 5.31 (d, \( J = 2.9 \) Hz, 1H), 3.94 (dd, \( J = 18.1, 2.8 \) Hz, 1H), 3.79 (d, \( J = 2.8 \) Hz, 1H), 3.07 (dd, \( J = 18.1, 2.8 \) Hz, 1H), 1.48 (d, \( J = 3.0 \) Hz, 9H), 1.32 (d, \( J = 3.0 \) Hz, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 174.8, 154.5, 154.1, 148.4, 136.3, 136.2, 135.1, 135.0, 134.9, 134.8, 131.7, 130.3, 129.6, 129.2, 129.0, 128.8, 128.7, 128.5, 126.8, 126.3, 123.8, 121.8, 116.9, 113.8, 112.5, 80.0, 74.6, 59.2, 56.2, 41.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) \( \nu \): 747, 763, 805, 833, 915, 1010, 1107, 1154, 1235, 1310, 1359, 1441, 1484, 1562, 2220, 2875, 2959, 3070, 3626 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{40}\)H\(_{37}\)ClN\(_2\)O\(_2\) [M + H]\(^+\) 613.2676; Found 613.2669.

**2-(2-(4-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3az)**

![3az](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. \( R_f = 0.33 \) (petroleum ether/ethyl acetate = 20:1). Yellow solid, 94.6 mg, 96% yield (two isomers), 13:1 dr, reaction time = 36 h, m.p. 214.5-215.1 °C.\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.57 (dd, \( J = 8.2, 2.8 \) Hz, 1H), 7.66 (td, \( J = 7.5, 2.8 \) Hz, 1H), 7.54 (td, \( J = 8.0, 2.6 \) Hz, 1H), 7.47 (dd, \( J = 7.9, 2.6 \) Hz, 1H), 7.35 – 7.29 (m, 4H), 7.26 (d, \( J = 3.2 \) Hz, 1H), 7.09 (dd, \( J = 8.3, 2.8 \) Hz, 1H), 6.99 (d, \( J = 8.3, 2.8 \) Hz, 1H).
= 7.6 Hz, 1H), 6.94 (td, \(J = 7.4, 2.7\) Hz, 1H), 6.81 (s, 1H), 6.56 (s, 1H), 6.06 (d, \(J = 2.9\) Hz, 1H), 5.31 (d, \(J = 2.9\) Hz, 1H), 3.95 (dd, \(J = 18.0, 2.8\) Hz, 1H), 3.79 (d, \(J = 2.8\) Hz, 1H), 3.07 (dd, \(J = 18.1, 2.8\) Hz, 1H), 1.49 (d, \(J = 3.0\) Hz, 9H), 1.32 (d, \(J = 3.0\) Hz, 9H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 174.7, 154.5, 154.1, 148.4, 136.3, 136.2, 135.4, 135.1, 134.9, 131.9, 131.8, 131.7, 130.5, 129.5, 129.2, 128.8, 128.7, 128.5, 126.8, 126.3, 123.8, 123.2, 121.8, 116.9, 113.8, 112.5, 80.1, 74.7, 59.2, 56.2, 41.1, 34.5, 34.3, 30.4, 30.3, 30.1. IR (KBr) \(\nu\): 762, 829, 919, 1008, 1079, 1117, 1233, 1308, 1359, 1443, 1482, 1567, 2222, 2874, 2959, 3070, 3626 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{40}\)H\(_{37}\)BrN\(_2\)O\(_2\) [M + H\(^+\)] 657.2111; Found 657.2113.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-(trifluoromethyl)phenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aa')

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. \(R_f = 0.45\) (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.0 mg, 53% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 257.5-258.1 \(^\circ\)C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.59 (d, \(J = 8.2\) Hz, 1H), 7.67 (t, \(J = 7.4\) Hz, 1H), 7.61 (d, \(J = 8.4\) Hz, 2H), 7.53 (d, \(J = 8.2\) Hz, 3H), 7.47 (d, \(J = 7.6\) Hz, 1H), 7.31 – 7.25 (m, 1H), 7.09 (d, \(J = 8.1\) Hz, 1H), 7.00 (dd, 1H), 6.95 (t, \(J = 7.3\) Hz, 1H), 6.82 (d, \(J = 2.0\) Hz, 1H), 6.57 (d, \(J = 2.3\) Hz, 1H), 6.16 (s, 1H), 5.32 (s, 1H), 3.93 (d, \(J = 18.0\) Hz, 1H), 3.81 (s, 1H), 3.09 (d, \(J = 18.0\) Hz, 1H), 1.49 (s, 9H), 1.32 (s, 9H).

\(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 174.6, 154.3, 154.2, 148.3, 140.3, 136.3, 136.1, 135.2, 134.9, 131.7, 129.5, 129.3, 129.2, 128.8, 128.7, 128.6, 128.6, 128.3, 126.3, 125.7 (q, \(J = 3.6\) Hz), 123.7, 121.9, 116.8, 113.7, 112.5, 80.0, 77.5, 77.2, 76.8, 74.6, 59.1, 56.1, 41.0, 34.5, 34.3, 30.4, 30.1. IR (KBr) \(\nu\): 763, 845, 932, 1010, 1068, 1125, 1165, 1233,
2-(2-(4-cyanophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ab')

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.20 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 73.2 mg, 80% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 233.0-234.0 °C. 1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 4.6 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.06 (t, J = 7.6 Hz, 3H), 6.98 (t, J = 7.7 Hz, 2H), 6.70 (s, 1H), 6.30 (s, 1H), 5.34 (s, 1H), 4.97 (s, 1H), 3.50 (d, J = 18.8 Hz, 1H), 3.26 (d, J = 18.8 Hz, 1H), 1.27 (d, J = 53.6 Hz, 18H). 13C NMR (125MHz, CDCl_3) δ 180.4, 154.4, 153.4, 151.1, 141.5, 136.7, 135.6, 132.4, 130.5, 128.7, 128.3, 127.8, 126.6, 125.6, 124.9, 123.6, 121.8, 118.3, 117.0, 115.0, 113.5, 112.9, 79.0, 76.0, 58.7, 52.5, 34.2, 34.0, 30.2. IR (KBr) ν: 763, 1042, 1125, 1231, 1307, 1363, 1438, 1476, 1550, 1707, 2223, 2959, 3074, 3615 cm⁻¹. HRMS (ESI, m/z): calculated for C_{41}H_{37}F_{3}N_{2}O_{2} [M + H]^+: 604.2959, found:604.2965.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxy-2-methylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ac')
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.30 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 83.6 mg, 90% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 221.1-221.9 °C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.59 (d, \( J = 8.1\) Hz, 1H), 7.70 (t, \( J = 7.4\) Hz, 1H), 7.58 (t, \( J = 7.7\) Hz, 1H), 7.53 (d, \( J = 7.6\) Hz, 1H), 7.30 – 7.21 (m, 1H), 7.07 (d, \( J = 8.0\) Hz, 1H), 7.03 – 6.96 (m, 1H), 6.93 (td, \( J = 7.4, 1.2\) Hz, 1H), 6.87 (d, \( J = 2.4\) Hz, 2H), 6.57 (d, \( J = 2.0\) Hz, 1H), 6.53 (d, \( J = 8.6\) Hz, 1H), 6.48 (dd, \( J = 8.6, 2.6\) Hz, 1H), 6.06 (s, 1H), 5.29 (s, 1H), 4.14 (d, \( J = 18.2\) Hz, 1H), 3.81 (s, 1H), 3.76 (s, 3H), 3.17 (d, \( J = 18.2\) Hz, 1H), 2.55 (s, 3H), 1.49 (s, 9H), 1.33 (s, 9H). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 175.7, 159.9, 155.2, 153.9, 148.3, 142.1, 136.5, 136.0, 134.8, 134.7, 131.9, 129.9, 129.1, 128.7, 128.4, 127.2, 127.1, 126.2, 125.8, 124.4, 121.7, 117.8, 116.8, 113.9, 111.7, 110.3, 79.9, 72.7, 58.6, 57.2, 55.2, 42.2, 34.5, 34.3, 30.4, 30.1, 19.8. IR (KBr) \( \nu \) : 732, 763, 807, 909, 998, 1044, 1123, 1156, 1235, 1305, 1360, 1443, 1471, 1572, 1613, 2286, 2960, 3072, 3631 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{42}\)H\(_{42}\)N\(_2\)O\(_3\) [M + H]\(^+\) 623.3268; Found 623.3264.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2,4-dimethylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ad')

![Diagram of the compound](image-url)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 86.1 mg, 95% yield (two isomers), 14:1 dr, reaction time = 36 h, m.p. 274.8-275.6 °C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.58 (d, \( J = 8.1\) Hz, 1H), 7.69 (t, \( J = 7.4\) Hz, 1H), 7.57 (t, \( J = 7.7\) Hz, 1H), 7.53 (d, \( J = 7.6\) Hz, 1H), 7.27 – 7.20 (m, 1H), 7.12 (s, 1H), 7.06 (d, \( J = 8.2\) Hz, 1H), 6.98 (d, \( J = 6.8\) Hz, 1H), 6.92 (t, \( J = 7.4\) Hz, 1H),
6.85 (d, J = 1.8 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 6.56 (d, J = 1.8 Hz, 1H), 6.47 (d, J = 7.9 Hz, 1H), 6.07 (s, 1H), 5.27 (s, 1H), 4.14 (d, J = 18.2 Hz, 1H), 3.79 (s, 1H), 3.16 (d, J = 18.2 Hz, 1H), 2.52 (s, 3H), 2.27 (s, 3H), 1.48 (s, 9H), 1.31 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 175.8, 155.3, 153.9, 148.3, 140.1, 139.2, 136.6, 136.0, 134.8, 134.7, 132.9, 131.9, 130.5, 129.9, 129.1, 128.7, 128.7, 128.4, 127.1, 126.2, 126.0, 125.9, 124.4, 121.7, 116.8, 113.9, 111.7, 79.8, 72.9, 58.6, 57.1, 42.1, 34.5, 34.3, 30.4, 30.1, 21.2, 19.4. IR (KBr) \(\upsilon\): 729, 765, 827, 910, 1003, 1032, 1122, 1161, 1235, 1311, 1374, 1441, 1474, 1569, 2223, 2875, 2960, 3070, 3627 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{42}\)H\(_{42}\)N\(_2\)O\(_2\) [M + H]\(^{+}\) 607.3319; Found 607.3317.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(5-fluoro-2-methylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ae')

![Chemical structure](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R\(_f\) = 0.43 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.1 mg, 99% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 225.7-226.5 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.60 (d, J = 8.1 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.07 (d, J = 8.2 Hz, 1H), 7.02-6.93 (m, 3H), 6.85 (d, J = 2.2 Hz, 1H), 6.58 (d, J = 2.2 Hz, 1H), 6.34 (dd, J = 10.0, 2.6 Hz, 1H), 6.08 (s, 1H), 5.30 (s, 1H), 4.10 (d, J = 18.3 Hz, 1H), 3.82 (s, 1H), 3.19 (d, J = 18.3 Hz, 1H), 2.53 (s, 3H), 1.49 (s, 9H), 1.32 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 175.2, 160.2 (d, J = 243.5 Hz), 155.0, 154.0, 147.9, 136.3, 135.9 (d, J = 3.2 Hz), 135.2 (d, J = 6.8 Hz) 134.8, 133.2 (d, J = 7.7 Hz), 131.9, 129.7, 129.1, 129.0, 128.7, 128.5, 127.1, 126.2, 124.3, 122.0, 116.7, 115.9 (d, J = 20.4 Hz), 113.7, 113.4 (d, J = 22.8 Hz) 111.7, 79.8, 72.7, 72.7, 58.4, 57.2, 41.8, 34.5, 34.3,
30.4, 30.0, 18.8. IR (KBr) ν: 742, 824, 900, 1008, 1122, 1157, 1239, 1310, 1364, 1440, 1473, 1572, 2222, 2875, 2958, 3070, 3632 cm⁻¹. HRMS (ESI) m/z: Calcd for C₄₁H₃₉FN₂O₂ [M + H]⁺ 611.3068; Found 611.3065.

2-(2-(2-bromo-5-fluorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3af')

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. Rᵣ = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.0 mg, 96% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 257.5-258.1 °C.¹H NMR (500 MHz, CDCl₃) δ 8.59 (d, J = 8.2 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.59 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.00-6.94 (m, 3H), 6.90 (d, J = 2.1 Hz, 1H), 6.55 (d, J = 2.2 Hz, 1H), 6.44 (dd, J = 9.3, 2.9 Hz, 1H), 6.16 (s, 1H), 5.30 (s, 1H), 4.04 (d, J = 18.2 Hz, 1H), 3.82 (s, 1H), 3.20 (d, J = 18.3 Hz, 1H), 1.48 (s, 9H), 1.32 (s, 9H).¹³C NMR (125 MHz, CDCl₃) δ 174.6, 160.9 (d, J = 247.5 Hz), 154.9, 154.1, 147.7, 136.3 (d, J = 6.7 Hz), 136.2, 136.1, 136.0 (d, J = 8.0 Hz), 135.2, 134.8, 131.8, 129.5, 129.1, 129.0, 128.9, 128.6, 127.2, 126.3, 124.3, 122.6 (d, J = 3.3 Hz), 122.1, 117.7 (d, J = 22.1 Hz), 116.9, 115.4 (d, J = 24.3 Hz), 113.6, 111.4, 80.0, 74.8, 58.6, 57.3, 41.6, 34.6, 34.4, 30.4, 30.1. IR (KBr) ν: 744, 823, 898, 1027, 1121, 1161, 1237, 1311, 1365, 1441, 1473, 1572, 2222, 2875, 2958, 3070, 3632 cm⁻¹. HRMS (ESI) m/z: Calcd for C₄₀H₃₆BrFN₂O₂ [M + H]⁺ 675.2017; Found 675.2019.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(naphthalen-1-yl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ag')
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. \( R_f = 0.40 \) (petroleum ether/ethyl acetate = 20:1). Yellow solid, 92.1 mg, 98% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 226.9-227.5 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.60 (d, \( J \) = 8.1 Hz, 1H), 7.86 (d, \( J \) = 8.7 Hz, 1H), 7.82 (d, \( J \) = 7.9 Hz, 1H), 7.77 (s, 1H), 7.72 (d, \( J \) = 8.0 Hz, 1H), 7.66 (t, \( J \) = 7.4 Hz, 1H), 7.61 (dd, \( J \) = 8.7, 1.7 Hz, 1H), 7.53 (t, \( J \) = 7.7 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.48 – 7.41 (m, 1H), 7.33 – 7.26 (m, 1H), 7.15 (d, \( J \) = 8.0 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.96 (t, \( J \) = 7.0 Hz, 1H), 6.90 (d, \( J \) = 2.0 Hz, 1H), 6.60 (d, \( J \) = 2.4 Hz, 1H), 6.29 (s, 1H), 5.32 (s, 1H), 4.15 (d, \( J \) = 17.9 Hz, 1H), 3.84 (s, 1H), 3.14 (d, \( J \) = 17.9 Hz, 1H), 1.51 (s, 9H), 1.36 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 175.0, 154.7, 154.1, 148.6, 136.3, 134.9, 134.8, 133.7, 133.3, 132.8, 131.7, 129.7, 129.2, 128.8, 128.7, 128.6, 128.5, 127.9, 127.6, 126.9, 126.8, 126.6, 126.4, 126.2, 123.9, 121.7, 116.9, 113.9, 112.6, 80.1, 75.3, 59.5, 56.3, 41.3, 34.5, 34.3, 30.4, 30.2. IR (KBr) \( \nu \): 740, 812, 863, 898, 1005, 1119, 1157, 1231, 1310, 1362, 1441, 1478, 1567, 2219, 2875, 2959, 3059, 3627 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{44}\)H\(_{40}\)N\(_2\)O\(_2\) [M + H]\(^+\) 629.3163; Found 629.3167.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(pyridin-2-yl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ah')
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. \( R_f = 0.30 \) (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.1 mg, 96% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 230.6-231.4 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta 8.55 \) (d, \( J = 8.1 \) Hz, 1H), 8.31-8.29 (m, 2H), 7.62 (td, \( J = 7.5, 1.1 \) Hz, 1H), 7.50 (t, \( J = 7.8 \) Hz, 1H), 7.44 (d, \( J = 7.6 \) Hz, 1H), 7.31 – 7.21 (m, 1H), 7.24 – 7.17 (m, 1H), 7.10 (d, \( J = 8.3 \) Hz, 1H), 7.00 (dd, \( J = 7.7, 1.4 \) Hz, 1H), 6.98 – 6.89 (m, 1H), 6.85 (d, \( J = 2.1 \) Hz, 1H), 6.56 (d, \( J = 2.3 \) Hz, 1H), 6.19 (s, 1H), 5.28 (s, 1H), 4.38 (d, \( J = 16.8 \) Hz, 1H), 3.78 (s, 1H), 2.97 (d, \( J = 16.8 \) Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H). \( ^{13}C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 177.7, 155.9, 154.6, 153.8, 149.7, 148.0, 136.9, 136.7, 136.5, 135.9, 134.7, 134.3, 131.8, 130.2, 129.0, 128.4, 128.3, 127.9, 126.5, 126.0, 125.9, 124.2, 123.6, 121.7, 116.8, 114.3, 113.0, 77.9, 75.8, 59.0, 55.5, 42.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) \( \nu: \) 765, 808, 861, 904, 998, 1043, 1123, 1156, 1236, 1305, 1360, 1443, 1488, 1572, 1612, 2224, 2878, 2959, 3070, 3626 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{39}\)H\(_{37}\)N\(_3\)O\(_2\) \([M + H]^+\) 580.2959; Found 580.2956.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methyl-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ba)

\[ \text{HO} \quad \text{CH}_3 \]
\[ \text{t-Bu} \quad \text{t-Bu} \]
\[ \text{NC} \quad \text{CN} \]

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. \( R_f = 0.38 \) (petroleum ether/ethyl acetate = 20:1). Yellow solid, 81.1 mg, 83% yield (two isomers), 9:1 dr, reaction time = 36 h, m.p. 236.3-237.0 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta 8.57 \) (d, \( J = 8.1 \) Hz, 1H), 7.65 (t, \( J = 7.4 \) Hz, 1H), 7.52 (t, \( J = 7.7 \) Hz, 1H), 7.46 (d, \( J = 7.6 \) Hz, 1H), 7.34 (td, \( J = 8.6, 7.0, 4.0 \) Hz, 5H), 7.06 (dd, \( J = 8.4, 1.8 \) Hz, 1H), 6.99 (d, \( J = 8.4 \) Hz, 1H), 6.88 (d, \( J = 2.0 \) Hz, 1H), 5.28 (s, 1H), 4.38 (d, \( J = 16.8 \) Hz, 1H), 3.78 (s, 1H), 2.97 (d, \( J = 16.8 \) Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H). \( ^{13}C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 177.7, 155.9, 154.6, 153.8, 149.7, 148.0, 136.9, 136.7, 136.5, 135.9, 134.7, 134.3, 131.8, 130.2, 129.0, 128.4, 128.3, 127.9, 126.5, 126.0, 125.9, 124.2, 123.6, 121.7, 116.8, 114.3, 113.0, 77.9, 75.8, 59.0, 55.5, 42.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) \( \nu: \) 765, 808, 861, 904, 998, 1043, 1123, 1156, 1236, 1305, 1360, 1443, 1488, 1572, 1612, 2224, 2878, 2959, 3070, 3626 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{39}\)H\(_{37}\)N\(_3\)O\(_2\) \([M + H]^+\) 580.2959; Found 580.2956.
Hz, 1H), 6.79 (s, 1H), 6.56 (d, J = 1.9 Hz, 1H), 6.07 (s, 1H), 5.31 (s, 1H), 4.02 (d, J = 18.0 Hz, 1H), 3.74 (s, 1H), 3.07 (d, J = 18.0 Hz, 1H), 2.22 (s, 3H), 1.50 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 175.2, 154.0, 152.6, 148.7, 136.3, 136.3, 136.2, 134.8, 134.8, 131.6, 130.8, 129.8, 129.3, 129.2, 128.9, 128.7, 128.6, 128.6, 127.6, 126.8, 126.2, 123.4, 116.6, 114.0, 112.4, 79.9, 75.2, 59.3, 56.4, 41.3, 34.5, 34.3, 30.4, 30.2, 20.6. IR (KBr) v: 730, 768, 813, 898, 1008, 1148, 1236, 1305, 1364, 1438, 1492, 1560, 2218, 2874, 2874, 2960, 3627 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{41}$H$_{40}$N$_2$O$_2$ [M + H]$^+$ 593.3163; Found 593.3168.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-fluoro-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ca)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R$_f$ = 0.35 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 79.6 mg, 89% yield (two isomers), 13:1 dr, reaction time = 36 h, m.p. 239.8-240.9 °C.$^1$H NMR (500 MHz, CDCl$_3$) δ 8.56 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.33 (s, 5H), 7.05 (dd, J = 9.1, 4.8 Hz, 1H), 6.97 (td, J = 8.9, 8.5, 3.0 Hz, 1H), 6.84 (d, J = 2.1 Hz, 1H), 6.70 (dd, J = 8.8, 2.9 Hz, 1H), 6.53 (d, J = 2.0 Hz, 1H), 6.06 (s, 1H), 5.31 (s, 1H), 4.02 (d, J = 17.9 Hz, 1H), 3.74 (s, 1H), 3.04 (d, J = 18.0 Hz, 1H), 1.47 (s, 9H), 1.33 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 174.9, 157.5 (d, J = 240.0 Hz), 154.2, 150.9, 150.9, 148.3, 136.3, 136.2, 136.0, 135.0, 129.2, 129.1, 128.9, 128.8, 128.8, 126.9, 126.3, 125.0 (d, J = 7.3 Hz), 118.1 (d, J = 8.1 Hz), 117.2 (d, J = 22.9 Hz), 115.8 (d, J = 23.5 Hz) 113.8, 112.4, 80.1, 75.5, 59.0, 56.4, 41.3, 34.6, 34.3, 30.3, 30.1. IR (KBr) v: 732, 766, 808, 904, 1016, 1145, 1230, 1311, 1373, 1436, 1489, 1554, 1606, 2219, 2876, 2958,
2-(6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3da)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R<sub>f</sub> = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.7 mg, 93% yield (two isomers), 12:1 dr, reaction time = 36 h, m.p. 248.4-249.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.57 (d, <i>J</i> = 8.2 Hz, 1H), 7.66 (t, <i>J</i> = 7.4 Hz, 1H), 7.53 (t, <i>J</i> = 7.6 Hz, 1H), 7.48 (d, <i>J</i> = 7.7 Hz, 1H), 7.34 (s, 5H), 7.22 (dd, <i>J</i> = 8.8, 2.4 Hz, 1H), 7.04 (d, <i>J</i> = 8.8 Hz, 1H), 6.99 (d, <i>J</i> = 2.3 Hz, 1H), 6.84 (d, <i>J</i> = 1.8 Hz, 1H), 6.55 (d, <i>J</i> = 1.7 Hz, 1H), 6.10 (s, 1H), 5.34 (s, 1H), 4.01 (d, <i>J</i> = 17.9 Hz, 1H), 3.74 (s, 1H), 3.02 (d, <i>J</i> = 17.9 Hz, 1H), 1.49 (s, 9H), 1.35 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.6, 154.3, 153.3, 148.2, 136.4, 136.1, 135.8, 135.1, 135.0, 130.9, 129.2, 129.1, 129.0, 128.8, 128.8, 128.8, 128.7, 128.5, 126.8, 126.4, 126.3, 125.4, 118.4, 113.8, 112.3, 80.1, 75.5, 58.9, 56.1, 41.2, 34.5, 34.3, 30.3, 30.2, 30.2, 30.1. IR (KBr) v: 737, 810, 907, 1014, 1145, 1237, 1309, 1373, 1438, 1479, 1554, 1594, 2217, 2876, 2959, 3064, 3606 cm<sup>-1</sup>. HRMS (ESI) m/z: Calcd for C<sub>40</sub>H<sub>37</sub>FN<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup> 597.2912; Found 597.2905.

2-(6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ea)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.37 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 82.4 mg, 84% yield (two isomers), 17:1 dr, reaction time = 36 h, m.p. 249.5-250.9 °C. 'H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.40 – 7.31 (m, 6H), 7.13 (d, J = 2.3 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 6.55 (d, J = 2.2 Hz, 1H), 6.10 (s, 1H), 5.34 (s, 1H), 4.00 (d, J = 17.9 Hz, 1H), 3.74 (s, 1H), 3.02 (d, J = 17.9 Hz, 1H), 1.49 (s, 9H), 1.36 (s, 9H). ^13C NMR (125 MHz, CDCl_3) δ 174.5, 154.3, 153.8, 148.2, 136.4, 136.1, 135.8, 135.1, 135.0, 133.9, 131.6, 129.2, 129.1, 128.9, 128.8, 128.8, 128.5, 126.8, 126.2, 126.0, 118.8, 113.8, 113.7, 112.3, 80.1, 75.5, 58.9, 56.0, 41.2, 34.5, 34.3, 30.3, 30.1. IR (KBr) ν: 732, 815, 908, 1009, 1235, 1301, 1359, 1438, 1470, 1565, 2223, 2874, 2959, 3069, 3616 cm⁻¹. HRMS (ESI) m/z: Calcd for C_{40}H_{37}BrN_2O_2 [M + H]^+ 657.2111; Found 657.2122.

5. Experimental procedure for gram scale synthesis of 3ax

A mixture of Cs_2CO_3 (0.6 mmol, 0.2 equiv.), 1x (3 mmol, 1.0 equiv.) and 2a (6 mmol, 2.0 equiv.) and 1,2-dichloroethane (30 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 25 °C in oil bath heating for the 24 h. Upon completion (monitored by TLC), the reaction solution was concentrated in vacuo. The crude product was purified by column
chromatography on silica gel (eluent PE:DCM = 3:1) to afford products 3ax as a mixture of the major and minor diastereomers of 3ax in 93% yield (1.66 g).

6. General experimental procedures for synthesis of compounds 5

![Diagram of synthesis process]

A mixture of DIPEA (0.02 mmol, 0.2 equiv.), 1 (0.15 mmol, 1.5 equiv.) and 4 (0.10 mmol, 1.0 equiv.) and dichloromethane (1.0 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 40 °C in oil bath heating for the 120 h. Upon completion (monitored by TLC), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 1:2 to 1:3) to afford pure products 5.

2-(1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3''-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5aa)

![Structure of 5aa]

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.3 mg, 95% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 197.8-198.7 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.95 (dd, J = 7.3, 1.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.36 (dt, J = 7.7, 3.8 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.22 (t, J = 7.7 Hz, 1H), 6.57 (dd, J = 7.8, 0.9 Hz, 1H), 5.40 (d, J = 10.5 Hz, 1H), 4.86 – 4.75 (m, 1H), 3.88 (d, J = 15.3 Hz, 1H), 3.20 (d, J = 15.4 Hz, 1H), 3.14 (d, J = 8.8 Hz, 1H), 2.39 (s, 3H). ^13C NMR (125 MHz, CDCl_3) δ 176.2, 172.0, 147.9, 141.3, 136.0,
134.7, 133.8, 130.6, 130.4, 129.9, 129.2, 128.5, 127.7, 126.7, 126.4, 125.1, 123.9, 114.9, 113.3, 107.7, 78.9, 76.0, 73.6, 63.4 (q, J = 29.7 Hz) 46.8, 36.0, 25.9. 19F NMR (471 MHz, CDCl3) δ -74.14. IR (KBr) υ: 695, 743, 862, 971, 1020, 1137, 1235, 1286, 1373, 1438, 1561, 1614, 1707, 2219, 2934, 2969, 3065, 3327 cm⁻¹. HRMS (ESI, m/z): calculated for C30H21F3N4O [M + Na]⁺: 533.1560, found:533.1563.

2-(5-methoxy-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-3(1H)-ylidene)malononitrile (5ab)

![Chemical structure of 5ab](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. Rf = 0.20 (petroleum ether/ethyl acetate = 2:1). Yellow solid, 44.2 mg, 83% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 106.7-107.5 °C. 1H NMR (500 MHz, CDCl3) δ 7.94 (dd, J = 7.4, 1.1 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 (t, J = 7.4 Hz, 1H), 7.26 (t, 3H), 7.24 (d, J = 8.5 Hz, 1H), 7.04 (dd, J = 8.5, 2.4 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 5.38 (d, J = 10.5 Hz, 1H), 4.84 – 4.75 (m, 1H), 3.79 (d, J = 15.0 Hz, 1H), 3.73 (s, 3H), 3.17 – 3.09 (m, 2H), 2.46 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 176.3, 172.2, 159.2, 141.3, 140.7, 137.0, 133.9, 130.7, 130.4, 129.8, 129.1, 128.4, 127.0, 126.7, 123.8, 123.5, 114.9, 113.5, 107.7, 107.4, 78.5, 76.1, 74.2, 63.4 (q, J = 29.6 Hz), 55.9, 46.8, 35.2, 29.8, 26.0. 19F NMR (471 MHz, CDCl3) δ -71.88. IR (KBr) υ: 710, 776, 837, 979, 1031, 1163, 1213, 1290, 1333, 1439, 1487, 1612, 1694, 2436, 2837, 2925, 3020, 3369 cm⁻¹. HRMS (ESI, m/z): calculated for C31H23F3N4O2 [M + Na]⁺: 563.1665, found:563.1659.

2-(1''-5-dimethyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-3(1H)-ylidene)malononitrile (5ac)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \( R_f = 0.23 \) (petroleum ether/ethyl acetate = 2:1). Yellow solid, 46.8 mg, 89% yield (two isomers), 10:1 dr, reaction time = 120 h, m.p. 221.5-222.3 °C.\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.94 (d, \( J = 7.3 \) Hz, 1H), 7.69 (s, 1H), 7.66 (d, \( J = 7.6 \) Hz, 2H), 7.41 (t, \( J = 7.7 \) Hz, 2H), 7.37 (t, \( J = 7.7 \) Hz, 1H), 7.32 (t, \( J = 7.4 \) Hz, 1H), 7.29 – 7.26 (m, 2H), 7.24 (d, \( J = 8.1 \) Hz, 1H), 6.58 (d, \( J = 7.7 \) Hz, 1H), 5.39 (d, \( J = 10.5 \) Hz, 1H), 4.85 – 4.75 (m, 1H), 3.82 (d, \( J = 15.2 \) Hz, 1H), 3.18 – 3.11 (m, 2H), 2.40 (s, 3H), 2.30 (s, 3H).\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 176.3, 172.1, 145.2, 141.3, 137.8, 136.2, 135.9, 133.9, 130.6, 130.4, 129.9, 129.8, 129.1, 128.4, 126.7, 126.1, 124.9, 123.8, 115.0, 113.4, 107.7, 78.4, 76.0, 73.8, 63.4 (q, \( J = 29.9 \) Hz) 46.8, 35.5, 29.8, 25.8, 21.4.\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -74.12. IR (KBr) \( \nu \): 695, 740, 867, 1021, 1141, 1237, 1285, 1374, 1443, 1491, 1559, 1615, 1704, 2219, 2936, 2974, 3034, 3322 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{31}\)H\(_{23}\)F\(_3\)N\(_4\)O [M + Na]\(^+\): 547.1716, found:547.1717.

2-(5-fluoro-1"-methyl-2"-oxo-4"-phenyl-5"-(trifluoromethyl)dispiro[indene-2,3"-pyrrolidine-2',3"-indolin]-1(3H)-ylidene)malononitrile (5ad)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \( R_f = 0.27 \) (petroleum ether/ethyl acetate = 2:1). Yellow solid, 44.4 mg, 84% yield (two isomers), 5:1 dr, reaction time = 120 h, m.p. 207.6-208.9 °C.\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.97 – 7.90 (m, 2H), 7.67 – 7.62
(m, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.37 (td, J = 7.7, 1.2 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.29 – 7.26 (m, 1H), 7.07 – 7.02 (m, 1H), 6.92 (td, J = 8.7, 2.5 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 5.39 (d, J = 10.4 Hz, 1H), 4.83 – 4.75 (m, 1H), 3.89 (d, J = 15.6 Hz, 1H), 3.18 (d, J = 8.8 Hz, 1H), 3.13 (d, J = 8.8 Hz, 1H), 2.50 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 176.2, 176.2, 170.4, 166.4 (d, J = 260.2 Hz), 151.2 (d, J = 10.4 Hz), 141.3, 133.6, 132.2 (d, J = 2.4 Hz), 130.6, 130.4, 130.4, 129.8, 129.3, 128.6, 127.5 (d, J = 10.1 Hz), 126.8, 124.0, 115.8 (d, J = 23.5 Hz), 114.8, 113.4 (d, J = 22.7 Hz), 113.3, 107.8, 78.5, 75.9, 73.7, 63.3 (q, J = 29.9 Hz), 46.9, 35.9, 26.0. 19F NMR (471 MHz, CDCl3) δ -74.07, -102.45. IR (KBr) υ: 696, 754, 857, 1102, 1150, 1262, 1370, 1480, 1563, 1613, 1711, 2223, 2308, 2898, 2980, 3071, 3326 cm⁻¹. HRMS (ESI, m/z): calculated for C30H20F4N4O [M + H]⁺: 529.1646, found:529.1651.

2-(5-chloro-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ae)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. Rf = 0.37 (petroleum ether/ethyl acetate = 2:1). Yellow solid, 52.3 mg, 96% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 207.0-208.6 °C. 1H NMR (500 MHz, CDCl3) δ 7.93 (d, J = 1.3 Hz, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.42 (dd, J = 8.4, 7.0 Hz, 2H), 7.37 (td, J = 7.7, 1.2 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.25 (m, 1H), 7.22 – 7.16 (m, 1H), 6.59 (d, J = 7.6 Hz, 1H), 5.39 (d, J = 10.5 Hz, 1H), 4.86 – 4.74 (m, 1H), 3.87 (d, J = 15.5 Hz, 1H), 3.16 (d, J = 15.6 Hz, 1H), 3.11 (d, J = 8.7 Hz, 1H), 2.49 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 176.3, 170.5, 149.5, 141.3, 141.3, 134.5, 133.7, 130.6, 130.5, 129.82, 129.3, 128.7, 128.3, 126.9, 126.5, 126.2, 124.0, 114.7, 113.1, 107.9, 79.3, 76.0, 74.3, 63.4 (q, J = 29.8 Hz), 46.9, 35.9, 26.0. 19F NMR (471 MHz, CDCl3) δ -74.16. IR (KBr) υ: 695, 752, 861, 911, 1088, 1152, 1234, 1284, 1368, 1456, 1559, 1609, 1711, 2221, 2886, 2933,
2971, 3325 cm$^{-1}$. HRMS (ESI, m/z): calculated for C$_{30}$H$_{20}$ClF$_3$N$_4$O [M + H]$^+$: 545.1351, found: 545.1350.

2-(1''-methyl-2''-oxo-4''-(o-tolyl)-5''-(trifluoromethyl)dispiro[indene-2,3''-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5af)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. $R_f = 0.37$ (petroleum ether/ethyl acetate = 3:1). Yellow solid, 52.3 mg, 36% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 117.7-118.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 7.8$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.38 – 7.30 (m, 2H), 7.28 – 7.09 (m, 3H), 7.09 – 7.02 (m, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.91 (t, $J = 7.8$ Hz, 1H), 6.25 – 6.19 (m, 1H), 5.52 – 5.43 (m, 1H), 5.30 (d, $J = 9.6$ Hz, 1H), 3.11 (d, $J = 17.0$ Hz, 1H), 2.92 (s, 3H), 2.59 (d, $J = 4.2$ Hz, 1H), 2.51 (d, $J = 17.0$ Hz, 1H), 2.47 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 179.3, 178.8, 146.9, 143.0, 138.5, 137.2, 135.6, 135.2, 134.4, 131.1, 130.1, 129.5, 128.0, 127.7, 126.9, 126.8, 125.6, 124.3, 123.3, 122.9, 114.0, 112.8, 110.1, 107.6, 78.7, 75.9, 70.3, 63.5 (q, $J = 30.0$ Hz), 49.5, 42.8, 24.9, 17.5. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -71.97. IR (KBr) v: 690, 742, 873, 957, 1054, 1123, 1288, 1366, 1402, 1467, 1563, 1609, 1686, 2223, 2976, 3067, 3292 cm$^{-1}$. HRMS (ESI, m/z): calculated for C$_{31}$H$_{23}$F$_3$N$_4$O [M + Na]$^+$: 547.1716, found: 547.1725.

2-(4''-(2-fluorophenyl)-1''-methyl-2''-oxo-5''-(trifluoromethyl)dispiro[indene-2,3''-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ag)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \( R_f = 0.40 \) (petroleum ether/ethyl acetate = 3:1). Yellow solid, 32.8 mg, 62% yield (two isomers), 5:1 dr, reaction time = 120 h, m.p. 184.3-185.1 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.90 (td, 1H), 7.85 – 7.80 (m, 2H), 7.44 (t, \( J = 7.5 \) Hz, 1H), 7.38 – 7.28 (m, 3H), 7.22 (t, \( J = 7.6 \) Hz, 2H), 7.20 – 7.10 (m, 2H), 6.50 (d, \( J = 7.7 \) Hz, 1H), 5.37 (d, \( J = 10.3 \) Hz, 1H), 5.33 – 5.20 (m, 1H), 3.90 (d, \( J = 15.8 \) Hz, 1H), 3.08 (d, \( J = 8.1 \) Hz, 1H), 2.93 (dd, \( J = 15.8, 3.7 \) Hz, 1H), 2.46 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 176.6, 173.0, 161.3 (d, \( J = 246.6 \) Hz), 147.9, 141.5, 135.9, 134.6, 132.5 (d, \( J = 3.9 \) Hz), 130.8, 130.7, 130.4, 130.2, 127.7, 126.1, 125.9, 125.4, 125.4, 125.3, 123.6, 121.6 (d, \( J = 10.3 \) Hz), 117.1 (d, \( J = 24.2 \) Hz), 114.6, 113.4, 107.8, 78.8, 75.5, 73.6, 61.2 (d, \( J = 30.0 \) Hz), 44.9, 37.9, 25.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -74.56, -105.34. IR (KBr) \( \nu \): 691, 752, 880, 1049, 1091, 1234, 1290, 1380, 1454, 1562, 1617, 1708, 2219, 2888, 2974, 3324 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{30}\)H\(_{20}\)F\(_4\)N\(_4\)O \([\text{M + H}]^+\) 529.1646; Found 529.1646.

2-(1''-methyl-2''-oxo-5''-(trifluoromethyl)-4''-(2-(trifluoromethyl)phenyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ah)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \( R_f = 0.25 \) (petroleum ether/ethyl acetate = 3:1). Yellow solid, 18.7 mg, 32% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 158.2-159.9 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.19 (d, \( J = 8.0 \) Hz, 1H), 7.76 – 7.68 (m, 2H), 7.61 (d, \( J = 8.2 \) Hz, 1H), 7.46 (t, \( J = 7.7 \) Hz, 1H), 7.38 – 7.32 (m, 1H), 7.22 (td, \( J = 7.5, 0.9 \) Hz, 1H), 7.09 – 7.03 (m, 2H), 6.95 (d, \( J = 7.6 \) Hz, 1H), 6.90 (t, \( J = 7.8 \) Hz, 1H), 6.28 – 6.21 (m, 1H), 5.58 – 5.47 (m, 1H), 5.35 (d, \( J = 9.2 \) Hz, 1H), 3.04 (d, \( J = 16.7 \) Hz, 1H), 2.96 (s, 3H), 2.64 (d, \( J = 4.3 \) Hz, 1H), 2.45 (d, \( J = 16.7 \) Hz, 1H).
13C NMR (125 MHz, CDCl3) δ 179.2, 175.9, 146.0, 142.9, 136.2, 135.4, 134.1, 132.6, 132.1, 130.3, 128.2, 127.8, 126.6, 126.4 (q, J = 5.9 Hz) 125.8, 124.4, 123.1, 123.0, 114.1, 112.3, 107.7, 79.4, 75.4, 70.6, 64.9 (q, J = 30.5 Hz), 44.1, 43.3, 25.9. 19F NMR (471 MHz, CDCl3) δ -57.66, -71.63. IR (KBr) v: 683, 758, 874, 1059, 1123, 1160, 1235, 1308, 1360, 1446, 1566, 1610, 1692, 2224, 2869, 2933, 3072, 3295 cm⁻¹. HRMS (ESI, m/z): calculated for C31H26F6N4O [M + H]+: 579.1614, found:579.1623.

2-(4′-(3-methoxyphenyl)-1′'-methyl-2′'-oxo-5′-(trifluoromethyl)dispiro[indene-2,3′-pyrrolidine-2′,3″-indolin]-1(3H)-ylidene)malononitrile (5ai)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. Rf = 0.28 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 53.6 mg, 99% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 188.5-189.3 °C. 1H NMR (400 MHz, CDCl3) δ 7.92 (dd, J = 11.5, 7.7 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.27 (d, J = 7.8 Hz, 2H), 7.20 (t, J = 8.2 Hz, 2H), 6.86 (dd, J = 8.3, 2.3 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 5.35 (d, J = 10.5 Hz, 1H), 4.84 – 4.66 (m, 1H), 3.87 (d, J = 15.5 Hz, 1H), 3.82 (s, 3H), 3.24 (d, J = 15.3 Hz, 1H), 3.13 (d, J = 8.9 Hz, 1H), 2.39 (s, 3H). 13C NMR (125MHz, CDCl3) δ 176.2, 172.1, 160.0, 147.9, 141.3, 136.0, 135.4, 134.7, 130.7, 130.4, 130.0, 127.7, 126.7, 126.7, 126.4, 125.1, 123.9, 121.9, 116.3, 115.0, 113.6, 113.3, 107.7, 78.8, 76.0, 73.6, 63.4 (q, J = 29.8 Hz), 55.5, 46.9, 36.1, 25.8. 19F NMR (471 MHz, CDCl3) δ -74.24. IR (KBr) v: 696, 745, 869, 1046, 1099, 1144, 1168, 1281, 1379, 1466, 1496, 1564, 1608, 1706, 2220, 2926, 2970, 3069, 3321 cm⁻¹. HRMS (ESI) m/z: Calcd for C31H23F3N4O2 [M + H]^+: 541.1846; Found 541.1844.

2-(1′'-methyl-2′'-oxo-4′- (m-tolyl)-5′-(trifluoromethyl)dispiro[indene-2,3′-pyrrolidine-2′,3″-indolin]-1(3H)-ylidene)malononitrile (5aj)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. $R_f = 0.33$ (petroleum ether/ethyl acetate = 3:1). Yellow solid, 51.5 mg, 98% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 181.4-182.1 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.3$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.49 – 7.41 (m, 3H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.33 – 7.23 (m, 2H), 7.22 (t, $J = 7.7$ Hz, 1H), 7.13 (d, $J = 7.5$ Hz, 1H), 6.57 (d, $J = 7.7$ Hz, 1H), 5.35 (d, $J = 10.4$ Hz, 1H), 4.85 – 4.73 (m, 1H), 3.87 (d, $J = 15.4$ Hz, 1H), 3.21 (d, $J = 15.3$ Hz, 1H), 3.14 (d, $J = 8.9$ Hz, 1H), 2.39 (d, $J = 2.9$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 176.3, 172.1, 147.9, 141.3, 138.8, 136.0, 134.6, 133.8, 130.7, 130.6, 130.4, 129.2, 128.9, 127.7, 126.9, 126.7, 126.4, 125.1, 123.8, 114.9, 113.4, 107.7, 78.8, 76.0, 73.6, 63.4 (q, $J = 29.7$ Hz), 46.8, 36.1, 25.8, 21.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.13. IR (KBr) $\nu$: 698, 745, 865, 973, 1050, 1104, 1141, 1168, 1282, 1378, 1467, 1563, 1614, 1709, 2222, 2930, 2973, 3067, 3327 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C$_{31}$H$_{23}$F$_3$N$_4$O $[M + H]^+$ 525.1897; Found 525.1895.

2-(4'-(3-fluorophenyl)-1''-methyl-2''-oxo-5''-(trifluoromethyl)dispiro[indene-2,3''-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ak)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. $R_f = 0.33$ (petroleum ether/ethyl acetate = 3:1). Yellow solid, 40.7 mg, 77% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 205.4-207.0 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.91 (dd, $J = 7.4$, 1.3 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.33 (m, 4H), 7.29 – 7.25 (m, 1H), 7.25 – 7.21 (m, 1H), 7.07 –
7.00 (m, 1H), 5.39 (d, J = 10.5 Hz, 1H), 4.81 – 4.70 (m, 1H), 3.89 (d, J = 15.3 Hz, 1H), 3.18 – 3.12 (m, 2H), 2.40 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 176.1, 171.8, 162.9 (d, J = 247.4 Hz), 147.6, 141.3, 136.4 (d, J = 7.2 Hz), 135.9, 134.8, 130.8 (d, J = 8.4 Hz), 130.5, 130.4, 127.9, 126.6, 126.4, 125.7 (d, J = 3.0 Hz), 125.2, 123.9, 117.0 (d, J = 22.7 Hz) 115.7 (d, J = 20.8 Hz) 114.9, 113.2, 107.8, 78.9, 76.0, 73.3, 63.5 (q, J = 30.0 Hz) 46.5, 36.0, 25.9. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -74.03, -110.05. IR (KBr) \(\nu\): 691, 756, 797, 864, 1020, 1102, 1145, 1238, 1374, 1447, 1489, 1568, 1610, 1707, 2221, 2877, 2937, 2973, 3068, 3338 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{30}\)H\(_{20}\)F\(_3\)N\(_4\)O [M + Na]\(^{+}\): 551.1465, found: 551.1479.

2-(4’-(3-chlorophenyl)-1''-methyl-2''-oxo-5’-( trifluoromethyl)dispiro[indene-2,3’-pyrrolidine-2’,3’-indolin]-1(3H)-ylidene)malononitrile (5al)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \(R_t = 0.35\) (petroleum ether/ethyl acetate = 3:1). Yellow solid, 51.2 mg, 94% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 169.7-170.8 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, J = 7.7 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 7.25 – 7.21 (m, 1H), 6.57 (d, J = 7.7 Hz, 1H), 5.37 (d, J = 10.5 Hz, 1H), 4.83 – 4.66 (m, 1H), 3.89 (d, J = 15.3 Hz, 1H), 3.14 (d, J = 6.6 Hz, 1H), 3.11 (s, 1H), 2.40 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 176.2, 171.8, 147.6, 141.3, 136.1, 136.0, 135.1, 134.8, 130.5, 130.5, 130.4, 129.9, 128.9, 128.3, 127.9, 126.6, 126.4, 125.2, 123.9, 114.8, 113.2, 107.8, 78.9, 76.0, 73.3, 63.6 (q, J = 30.0 Hz), 46.6, 36.1, 25.9. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -74.13. IR (KBr) \(\nu\): 693, 750, 797, 862, 1019, 1097, 1138, 1174, 1235, 1281, 1370, 1434, 1473, 1715, 2224, 2855, 2924, 2962, 3066, 3331 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{30}\)H\(_{20}\)Cl\(_3\)F\(_3\)N\(_4\)O [M + H]\(^{+}\): 545.1351; Found 545.1351.
2-(4′-(4-methoxyphenyl)-1''-methyl-2''-oxo-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5am)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.3 mg, 89% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 183.4-185.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (dd, \(J = 7.4, 1.2\) Hz, 1H), 7.90 (d, \(J = 8.1\) Hz, 1H), 7.62 – 7.53 (m, 2H), 7.46 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.19 (m, 2H), 6.98 – 6.87 (m, 2H), 6.57 (d, \(J = 7.6\) Hz, 1H), 5.36 (d, \(J = 10.6\) Hz, 1H), 4.80 – 4.66 (m, 1H), 3.86 (d, \(J = 15.3\) Hz, 1H), 3.79 (s, 3H), 3.22 (d, \(J = 15.4\) Hz, 1H), 3.15 (d, \(J = 8.8\) Hz, 1H), 2.39 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.2, 172.1, 159.4, 147.9, 141.2, 136.0, 134.7, 131.0, 130.7, 130.4, 127.7, 126.6, 126.4, 125.4, 125.1, 123.8, 114.9, 114.5, 113.3, 107.7, 78.8, 75.9, 73.8, 63.4 (q, \(J = 29.6\) Hz) 55.4, 46.2, 35.8, 25.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -71.95. IR (KBr) \(\nu:\) 688, 755, 844, 1045, 1141, 1174, 1234, 1272, 1375, 1463, 1518, 1561, 1612, 1711, 2220, 2928, 2973, 3071, 3352 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{31}\)H\(_{23}\)F\(_3\)N\(_4\)O\(_2\) [M + H]\(^+\): 541.1846, found: 541.1849.

2-(1''-methyl-2''-oxo-4'-(p-tolyl)-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5an)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.3 mg, 89% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 183.4-185.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (dd, \(J = 7.4, 1.2\) Hz, 1H), 7.90 (d, \(J = 8.1\) Hz, 1H), 7.62 – 7.53 (m, 2H), 7.46 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.19 (m, 2H), 6.98 – 6.87 (m, 2H), 6.57 (d, \(J = 7.6\) Hz, 1H), 5.36 (d, \(J = 10.6\) Hz, 1H), 4.80 – 4.66 (m, 1H), 3.86 (d, \(J = 15.3\) Hz, 1H), 3.79 (s, 3H), 3.22 (d, \(J = 15.4\) Hz, 1H), 3.15 (d, \(J = 8.8\) Hz, 1H), 2.39 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.2, 172.1, 159.4, 147.9, 141.2, 136.0, 134.7, 131.0, 130.7, 130.4, 127.7, 126.6, 126.4, 125.4, 125.1, 123.8, 114.9, 114.5, 113.3, 107.7, 78.8, 75.9, 73.8, 63.4 (q, \(J = 29.6\) Hz) 55.4, 46.2, 35.8, 25.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -71.95. IR (KBr) \(\nu:\) 688, 755, 844, 1045, 1141, 1174, 1234, 1272, 1375, 1463, 1518, 1561, 1612, 1711, 2220, 2928, 2973, 3071, 3352 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{31}\)H\(_{23}\)F\(_3\)N\(_4\)O\(_2\) [M + H]\(^+\): 541.1846, found: 541.1849.
ether/dichloromethane = 1:1-3:1 as eluent. R<sub>f</sub> = 0.35 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 49.6 mg, 95% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 195.4-196.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (dd, <i>J</i> = 7.4, 1.2 Hz, 1H), 7.90 (d, <i>J</i> = 8.1 Hz, 1H), 7.54 (d, <i>J</i> = 8.0 Hz, 2H), 7.45 (td, <i>J</i> = 7.5, 1.0 Hz, 1H), 7.36 (td, <i>J</i> = 7.6, 1.4 Hz, 2H), 7.27 (d, <i>J</i> = 7.6 Hz, 1H), 7.25 – 7.19 (m, 3H), 6.57 (d, <i>J</i> = 7.7 Hz, 1H), 5.37 (d, <i>J</i> = 10.5 Hz, 1H), 4.84 – 4.72 (m, 1H), 3.87 (d, <i>J</i> = 15.4 Hz, 1H), 3.21 (d, <i>J</i> = 15.4 Hz, 1H), 3.15 (d, <i>J</i> = 8.8 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 176.2, 172.0, 147.9, 141.2, 138.3, 136.0, 134.6, 130.7, 130.6, 130.4, 129.8, 129.7, 127.7, 126.7, 126.4, 125.1, 123.8, 114.9, 113.3, 107.7, 78.8, 76.0, 73.7, 63.4 (q, <i>J</i> = 29.5 Hz), 46.5, 35.9, 25.8, 21.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -74.18. IR (KBr) v: 693, 745, 862, 1020, 1137, 1170, 1234, 1284, 1374, 1438, 1465, 1520, 1557, 1614, 1706, 2218, 2930, 2972, 3066, 3328 cm<sup>-1</sup>. HRMS (ESI, m/z): calculated for C<sub>31</sub>H<sub>23</sub>F<sub>3</sub>N<sub>4</sub>O [M + H]+: 525.1897, found: 525.1890.

2-(4′-(4-fluorophenyl)-1′″-methyl-2′″-oxo-5′″-(trifluoromethyl)dispiro[indene-2,3′-pyrrolidine-2′,3″-indolin]-1(3H)-ylidene)malononitrile (5ao)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R<sub>f</sub> = 0.23 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.4 mg, 92% yield (two isomers), 12:1 dr, reaction time = 96 h, m.p. 216.5-217.4 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.86 (m, 2H), 7.68 – 7.61 (m, 2H), 7.47 (td, <i>J</i> = 7.5, 1.0 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.27 (d, <i>J</i> = 1.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.11 (t, <i>J</i> = 8.6 Hz, 2H), 6.57 (d, <i>J</i> = 7.7 Hz, 1H), 5.39 (d, <i>J</i> = 10.5 Hz, 1H), 4.83 – 4.62 (m, 1H), 3.88 (d, <i>J</i> = 15.2 Hz, 1H), 3.15 (d, <i>J</i> = 15.2 Hz, 1H), 3.11 (d, <i>J</i> = 8.7 Hz, 1H), 2.40 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.2, 176.2, 171.9, 162.50 (d, <i>J</i> = 249.0 Hz), 147.7, 141.3, 136.0, 134.8, 131.6 (d, <i>J</i> = 8.0 Hz), 130.5, 130.5,
129.6 (d, $J = 3.3$ Hz), 127.8, 126.6, 126.4, 125.2, 123.9, 116.2 (d, $J = 21.4$ Hz), 114.9, 113.2, 107.8, 78.8, 75.9, 73.4, 63.7 (q, $J = 29.7$ Hz) 46.2, 35.9, 25.9. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -74.13, -113.04. IR (KBr) $\nu$: 691, 746, 850, 1020, 1134, 1233, 1286, 1371, 1434, 1468, 1513, 1564, 1707, 2220, 2871, 2934, 3070, 3329 cm$^{-1}$. HRMS (ESI, m/z): calculated for C$_{30}$H$_{20}$F$_3$N$_4$O [M + H]$^+$: 529.1646, found: 529.1655.

2-(4''-(4-chlorophenyl)-1''-methyl-2''-oxo-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ap)

![结构式]

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R$_f$ = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.6 mg, 89% yield (two isomers), 11:1 dr, reaction time = 96 h, m.p. 198.1-199.3 °C.$^1$H NMR (500 MHz, CDCl$_3$) δ 7.91 (dt, $J = 8.0$, 1.8 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.43 – 7.33 (m, 4H), 7.26 (t, 1H), 7.23 (t, $J = 6.9$ Hz, 1H), 6.57 (d, $J = 7.7$ Hz, 1H), 5.38 (d, $J = 10.5$ Hz, 1H), 4.80 – 4.63 (m, 1H), 3.87 (d, $J = 15.2$ Hz, 1H), 3.15 – 3.08 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.2, 171.8, 147.6, 141.3, 135.9, 134.8, 134.6, 132.4, 131.2, 130.5, 129.4, 127.9, 126.6, 126.4, 125.2, 123.9, 114.9, 113.1, 107.8, 78.8, 75.9, 73.3, 63.5 (q, $J = 30.0$ Hz), 46.3, 35.9, 25.9. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -74.24. IR (KBr) $\nu$: 693, 749, 873, 1049, 1094, 1138, 1232, 1285, 1377, 1440, 1514, 1564, 1613, 1707, 2220, 2925, 2972, 3071, 3329 cm$^{-1}$. HRMS (ESI, m/z): calculated for C$_{30}$H$_{20}$ClF$_3$N$_4$O [M + Na]$^+$: 567.1170, found: 567.1166.

2-(4''-(4-bromophenyl)-1''-methyl-2''-oxo-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5aq)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R<sub>f</sub> = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 56.4 mg, 96% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 186.4-187.3 °C. ¹H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.85 (m, 2H), 7.54 (s, 4H), 7.47 (t, J = 7.5 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.25 (m, 1H), 7.23 (t, J = 6.7 Hz, 1H), 6.57 (d, J = 7.6 Hz, 1H), 5.36 (d, J = 10.5 Hz, 1H), 4.82 – 4.63 (m, 1H), 3.87 (d, J = 15.3 Hz, 1H), 3.17 – 3.06 (m, 2H), 2.40 (s, 3H). ¹³C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.2, 171.8, 147.6, 141.3, 136.0, 134.8, 132.9, 132.4, 131.5, 130.5, 130.5, 127.9, 126.7, 126.4, 125.22, 123.9, 122.8, 114.9, 113.1, 107.8, 78.9, 76.0, 73.3, 63.5 (q, J = 29.9 Hz), 46.4, 36.0, 25.9. ¹⁹F NMR (471 MHz, CDCl<sub>3</sub>) δ -74.25. IR (KBr) ν: 693, 754, 859, 1012, 1107, 1146, 1232, 1282, 1374, 1460, 1490, 1563, 1609, 1706, 2218, 2934, 2968, 3066, 3324 cm<sup>-1</sup>. HRMS (ESI, m/z): calculated for C<sub>30</sub>H<sub>20</sub>BrF<sub>3</sub>N<sub>4</sub>O [M + H]<sup>+</sup>: 589.0845, found: 589.0847.

2-(1''-methyl-4''-(naphthalen-1-yl)-2''-oxo-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ar)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R<sub>f</sub> = 0.30 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 37.6 mg, 67% yield (two isomers), 10:1 dr, reaction time = 96 h, m.p. 189.2-190.0 °C. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, J = 1.9 Hz, 1H), 8.00 (dd,
$J = 7.4, 1.3 \text{ Hz, 1H}), 7.90 \text{ (dd, } J = 8.8, 5.1 \text{ Hz, 3H}), 7.86 - 7.78 \text{ (m, 1H)}, 7.70 \text{ (dd, } J = 8.7, 2.0 \text{ Hz, 1H}), 7.55 - 7.47 \text{ (m, 2H)}, 7.43 \text{ (td, } J = 7.5, 1.0 \text{ Hz, 1H}), 7.38 \text{ (td, } J = 7.8, 1.3 \text{ Hz, 1H}), 7.35 - 7.27 \text{ (m, 2H)}, 7.20 \text{ (t, } J = 7.7 \text{ Hz, 1H}), 6.58 \text{ (dd, } J = 7.8, 1.0 \text{ Hz, 1H}), 5.59 \text{ (d, } J = 10.4 \text{ Hz, 1H}), 4.97 \text{ (s, 1H)}, 3.95 \text{ (d, } J = 15.4 \text{ Hz, 1H)}, 3.29 - 3.16 \text{ (m, 2H)}, 2.41 \text{ (s, 3H)}. \quad \delta$ 176.3, 172.1, 147.8, 141.3, 136.0, 134.8, 133.3, 132.9, 131.2, 130.6, 130.4, 129.9, 128.7, 128.4, 127.7, 127.6, 127.6, 127.0, 126.9, 126.9, 126.5, 126.3, 125.1, 123.9, 115.0, 113.3, 107.5, 78.9, 76.1, 73.8, 63.4 (q, $J = 28.1$ Hz), 47.0, 36.3, 25.8. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 176.3, 172.1, 147.8, 141.3, 136.0, 134.8, 133.3, 132.9, 131.2, 130.6, 130.4, 129.9, 128.7, 128.4, 127.7, 127.6, 127.6, 127.0, 126.9, 126.9, 126.5, 126.3, 125.1, 123.9, 115.0, 113.3, 107.8, 78.9, 76.1, 73.8, 63.4 (q, $J = 28.1$ Hz), 47.0, 36.3, 25.8. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -73.55. IR (KBr) $\nu$: 693, 756, 878, 1049, 1089, 1145, 1237, 1283, 1376, 1465, 1564, 1610, 1709, 2218, 2892, 2929, 2974, 3063, 3342 cm$^{-1}$. HRMS (ESI) m/z: Calcd for C34H23F3N4O $[M + H]^+$ 561.1897; Found 561.1894.

2-(1''-methyl-2''-oxo-4'-(pyridin-2-yl)-5'-(trifluoromethyl)dispiro[indene-2,3''-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5as)

![Chemical Structure](attachment:image.png)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. $R_f = 0.40$ (petroleum ether/ethyl acetate = 3:1). Yellow solid, 44.7 mg, 87% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 215.7-216.3 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.64 (dd, $J = 4.8, 1.8$ Hz, 1H), 8.00 (d, $J = 7.4$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.71 (td, $J = 7.7, 1.9$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.44 - 7.34 (m, 2H), 7.31 - 7.18 (m, 3H), 5.47 (d, $J = 10.1$ Hz, 1H), 5.29 - 5.15 (m, 1H), 3.97 (d, $J = 16.6$ Hz, 1H), 3.70 (d, $J = 16.5$ Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.4, 171.8, 153.9, 149.3, 148.7, 141.3, 137.4, 136.0, 134.7, 130.6, 130.4, 127.5, 126.7, 126.0, 124.9, 123.9, 123.1, 115.0, 113.3, 107.7, 78.3, 76.5, 74.1, 63.0 (q, $J = 29.9$ Hz), 47.9, 35.3, 25.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.38. IR (KBr) $\nu$: 694, 748, 864, 1021, 1104, 1141, 1233, 1287,
1376, 1438, 1470, 1615, 1712, 2219, 2943, 3067, 3324 cm\(^{-1}\). HRMS (ESI) m/z:
Calcd for C\(_{20}\)H\(_{30}\)F\(_3\)N\(_5\)O [M + H]\(^+\) 512.1693; Found 512.1693.

2-(7''-methoxy-1''-methyl-2''-oxo-4'-phenyl-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidine)malononitrile (5ba)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R\(_f\) = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 53.0 mg, 98% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 187.1-187.9 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 8.1\) Hz, 1H), 7.58 (d, \(J = 7.6\) Hz, 2H), 7.49 (d, \(J = 7.3\) Hz, 1H), 7.38 (t, \(J = 7.4\) Hz, 1H), 7.33 (t, \(J = 7.7\) Hz, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.13 (t, 1H), 6.87 (d, \(J = 8.3\) Hz, 1H), 5.30 (d, \(J = 10.5\) Hz, 1H), 4.78 – 4.67 (m, 1H), 3.80 (d, \(J = 15.3\) Hz, 1H), 3.72 (s, 3H), 3.08 (d, \(J = 15.3\) Hz, 1H), 3.05 (d, \(J = 8.8\) Hz, 1H), 2.56 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 176.4, 172.1, 147.8, 145.0, 136.0, 134.6, 133.9, 132.7, 129.9, 129.1, 128.6, 128.4, 127.7, 126.3, 125.2, 124.6, 119.5, 114.9, 114.6, 113.5, 78.4, 76.0, 73.6, 63.48 (q, \(J = 29.6\) Hz), 56.4, 46.7, 36.0, 29.2. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -73.89. IR (KBr) \(\nu\): 728, 768, 868, 947, 1050, 1143, 1280, 1364, 1462, 1495, 1561, 1607, 1704, 2220, 2846, 2939, 2967, 3072, 3340 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{31}\)H\(_{23}\)F\(_3\)N\(_4\)O\(_2\) [M + H]\(^+\): 541.1846, found: 541.1847.

2-(7''-fluoro-1''-methyl-2''-oxo-4'-phenyl-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidine)malononitrile (5ca)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 46.3 mg, 88% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 168.7-168.6 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, \(J = 8.1\) Hz, 1H), 7.75 (d, \(J = 7.4\) Hz, 1H), 7.65 (d, \(J = 7.7\) Hz, 2H), 7.48 (t, \(J = 7.4\) Hz, 1H), 7.42 (t, \(J = 7.7\) Hz, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.21 (td, \(J = 8.0, 4.6\) Hz, 1H), 7.10 (dd, \(J = 10.9, 8.7\) Hz, 1H), 5.37 (d, \(J = 10.4\) Hz, 1H), 4.86 – 4.76 (m, 1H), 3.86 (d, \(J = 15.4\) Hz, 1H), 3.20 (d, \(J = 15.3\) Hz, 1H), 3.13 (d, \(J = 8.5\) Hz, 1H), 2.60 (d, \(J = 2.6\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 176.0, 171.8, 147.7, 147.3 (d, \(J = 245.1\) Hz), 135.9, 134.9, 133.7 (d, \(J = 1.9\) Hz), 133.6, 129.8, 129.2, 128.6, 128.0, 127.6 (d, \(J = 8.3\) Hz), 126.4, 125.3, 124.6 (d, \(J = 6.2\) Hz), 122.7, 118.5 (d, \(J = 19.1\) Hz) 114.8, 113.2, 78.8, 76.0, 73.7, 63.4 (q, \(J = 29.8\) Hz, 46.7, 36.0, 28.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -74.33, -136.27. IR (KBr) \(\nu\): 564, 608, 717, 766, 875, 1055, 1137, 1247, 1283, 1345, 1370, 1476, 1603, 1632, 1717, 2222, 2858, 2938, 3067, 3337 cm\(^{-1}\). HRMS (ESI) m/z: Calcd for C\(_{30}\)H\(_{20}\)F\(_4\)N\(_4\)O [M + H\(^+\)] 529.1646; Found 529.1643.

**2-(7''-chloro-1''-methyl-2''-oxo-4''-phenyl-5''-(trifluoromethyl)dispiro[indene-2,3''-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5da)**

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate =
Yellow solid, 44.8 mg, 82% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 207.6-208.3 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 8.0\) Hz, 1H), 7.82 (d, \(J = 7.3\) Hz, 1H), 7.64 (d, \(J = 7.7\) Hz, 2H), 7.48 (t, \(J = 7.4\) Hz, 1H), 7.41 (t, \(J = 7.7\) Hz, 2H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.18 (t, \(J = 7.8\) Hz, 1H), 5.34 (d, \(J = 10.5\) Hz, 1H), 4.86 – 4.76 (m, 1H), 3.82 (d, \(J = 15.3\) Hz, 1H), 3.18 (d, \(J = 15.3\) Hz, 1H), 3.10 (d, \(J = 8.4\) Hz, 1H), 2.73 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 176.9, 171.9, 147.6, 137.0, 136.0, 134.9, 133.8, 133.6, 132.5, 129.8, 129.2, 128.6, 128.0, 126.3, 125.3, 125.0, 124.7, 115.4, 114.8, 113.2, 78.7, 75.6, 73.8, 63.4 (q, \(J = 29.9\) Hz), 46.6, 36.2, 29.3. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -74.29. IR (KBr) \(\nu\): 702, 763, 904, 1017, 1063, 1128, 1166, 1282, 1361, 1458, 1561, 1603, 1710, 2219, 2855, 2924, 3064, 3341 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{30}\)H\(_{20}\)ClF\(_3\)N\(_4\)O [M + H]\(^+\): 545.1351, found: 545.1350.

2-(7''-bromo-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ea)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \(R_f\) = 0.38 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 36.7 mg, 62% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 174.8-175.9 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 8.1\) Hz, 1H), 7.86 (d, \(J = 6.9\) Hz, 1H), 7.63 (d, \(J = 7.6\) Hz, 2H), 7.51 – 7.44 (m, 2H), 7.41 (t, \(J = 7.6\) Hz, 2H), 7.37 – 7.27 (m, 3H), 7.11 (t, \(J = 7.8\) Hz, 1H), 5.33 (d, \(J = 10.6\) Hz, 1H), 4.87 – 4.74 (m, 1H), 3.80 (d, \(J = 15.4\) Hz, 1H), 3.17 (d, \(J = 15.4\) Hz, 1H), 3.08 (d, \(J = 8.4\) Hz, 1H), 2.74 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 177.1, 171.9, 147.5, 138.5, 136.0, 135.8, 134.9, 134.2, 133.6, 129.8, 129.2, 128.6, 128.0, 126.3, 125.5, 125.4, 125.1, 114.8, 113.1,
102.1, 78.7, 75.6, 73.9, 63.4 (q, \( J = 30.3 \) Hz), 46.5, 36.3, 29.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -74.38. IR (KBr) \( \nu: \) 700, 854, 944, 1013, 1056, 1132, 1173, 1274, 1348, 1455, 1558, 1604, 1714, 2221, 2951, 3004, 3063, 3350 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{30}\)H\(_{20}\)BrF\(_3\)N\(_4\)O \([\text{M + H}^+]: \) 589.0845, found: 589.0845.

2-(1''-methyl-2''-oxo-4''-phenyl-5'',7''-bis(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5fa)

![Structure of 5fa](image)

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. \( R_f = 0.60 \) (petroleum ether/ethyl acetate = 3:1). Yellow solid, 36.4 mg, 63% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 202.2-203.3 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.12 (d, \( J = 7.4 \) Hz, 1H), 7.91 (d, \( J = 8.1 \) Hz, 1H), 7.64 (dd, \( J = 10.2, 8.3 \) Hz, 3H), 7.48 (t, \( J = 7.5 \) Hz, 1H), 7.42 (t, \( J = 7.6 \) Hz, 2H), 7.34 (dd, \( J = 7.8, 4.8 \) Hz, 3H), 7.30 – 7.24 (m, 1H), 5.36 (d, \( J = 10.6 \) Hz, 1H), 4.90 – 4.77 (m, 1H), 3.81 (d, \( J = 15.4 \) Hz, 1H), 3.20 (d, \( J = 15.4 \) Hz, 1H), 3.10 (d, \( J = 8.3 \) Hz, 1H), 2.57 (q, \( J = 2.3 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 177.7, 171.7, 147.3, 139.3, 135.9, 135.1, 133.7, 133.4, 129.8, 129.7, 129.2, 128.7, 128.1, 128.0 (q, \( J = 5.9 \) Hz), 126.3, 125.5, 123.3, 114.7, 112.9, 78.9, 74.5, 73.8, 63.2 (q, \( J = 29.9 \) Hz), 46.6, 36.2, 28.6, 28.6, 28.5, 28.4. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -53.32, -74.28. IR (KBr) \( \nu: \) 700, 770, 863, 958, 1128, 1174, 1273, 1341, 1458, 1556, 1600, 1737, 2220, 2897, 2973, 3067, 3341 cm\(^{-1}\). HRMS (ESI, m/z): calculated for C\(_{31}\)H\(_{20}\)F\(_6\)N\(_4\)O \([\text{M + H}^+]: \) 579.1646, found: 579.1642.

2-(5''-bromo-1''-methyl-2''-oxo-4''-phenyl-5''-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ga)
The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. $R_f = 0.13$ (petroleum ether/ethyl acetate = 3:1). Yellow solid, 52.6 mg, 89% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 196.4-197.2 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 1.8$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 2H), 7.51 (dd, $J = 8.2$, 1.9 Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.38 – 7.31 (m, 2H), 7.25 (d, $J = 10.5$ Hz, 1H), 6.48 (d, $J = 8.2$ Hz, 1H), 5.34 (d, $J = 10.5$ Hz, 1H), 4.83 – 4.73 (m, 1H), 3.85 (d, $J = 15.4$ Hz, 1H), 3.23 (d, $J = 15.6$ Hz, 1H), 3.13 (d, $J = 8.7$ Hz, 1H), 2.38 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.6, 171.4, 147.4, 140.3, 135.9, 134.9, 133.4, 133.2, 132.5, 130.0, 129.8, 129.2, 128.6, 127.9, 126.5, 125.1, 116.8, 114.5, 113.2, 109.2, 79.2, 76.1, 73.6, 63.3 (q, $J = 29.7$ Hz), 46.8, 35.8, 26.0. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.24. IR (KBr) $\nu$: 700, 733, 862, 1052, 1107, 1148, 1231, 1278, 1355, 1419, 1481, 1560, 1608, 1714, 2222, 2928, 2971, 3071, 3327 cm$^{-1}$. HRMS (ESI, m/z): calculated for C$_{30}$H$_{20}$BrF$_3$N$_4$O [M + H]$^+$: 589.0845, found: 589.0853.

7. Experimental procedure for gram scale synthesis of 5aa

A mixture of DIPEA (0.6 mmol, 0.2 equiv.), 1 (4.5 mmol, 1.5 equiv.) and 4 (3.0 mmol, 1.0 equiv.) and dichloromethane (30 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 40 °C for the 5 days. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 1:2 to 1:3) to afford products 5aa as a mixture of the major and minor diastereomers of 5aa in 95% yield (1.26 g).

8. Experimental procedures for synthesis of compound 6
Under a nitrogen atmosphere, \( \text{AlCl}_3 \) (0.5 mmol, 66.5 mg) was added to the solution of \( 3ax \) (0.1 mmol 59.7 mg) in anhydrous toluene (2 mL). Then, the reaction mixture was stirred at 50 °C for 3 hours. Next, another portion of \( \text{AlCl}_3 \) (0.5 mmol, 66.5 mg) was added to the reaction mixture. And the reaction solution was stirred overnight. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was quenched with water (5 mL). Subsequently, the reaction mixture was extracted with ethyl acetate (10 mL) and the organic layer was dried over anhydrous sodium sulfate. The resultant solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate = 10:1-5:1) to afford the pure product \( 6 \). \( R_f = 0.38 \) (petroleum ether/ethyl acetate = 3:1). Brown solid, 9.7 mg, 20% yield, m.p. 95.5-96.3 °C.\(^1\)H NMR (500 MHz, DMSO-\( d_6 \)) \( \delta \) 10.01 (s, 1H), 7.88 (d, \( J = 7.9 \) Hz, 1H), 7.81 – 7.77 (m, 2H), 7.58 (dd, \( J = 7.7, 1.7 \) Hz, 1H), 7.39-7.31 (m, 2H), 7.30 – 7.21 (m, 4H), 7.12 (td, \( J = 7.5, 1.2 \) Hz, 1H), 6.99 (d, \( J = 8.9 \) Hz, 1H), 6.92 – 6.90 (m, 2H), 6.87 (t, \( J = 8.8 \) Hz, 2H), 5.01 (s, 1H), 4.78 (s, 1H), 3.45 (d, \( J = 17.1 \) Hz, 1H), 2.65 (d, \( J = 16.9 \) Hz, 1H). \(^13\)C NMR (125 MHz, DMSO-\( d_6 \)) \( \delta \) 166.2, 161.6 (d, \( J = 244.2 \) Hz), 159.8, 156.3, 153.7, 148.9, 135.5, 133.5, 131.9 (d, \( J = 2.9 \) Hz), 131.6, 129.9, 129.1, 128.5 (d, \( J = 8.0 \) Hz), 127.4, 127.3, 125.4, 124.0, 121.7, 121.6, 116.9, 116.4, 115.0, 114.2 (d, \( J = 21.3 \) Hz), 96.3, 72.4, 60.7, 46.0, 35.6. IR (KBr) \( \nu \): 762, 830, 998, 1021, 1106, 1164, 1233, 1279, 1380, 1458, 1510, 1550, 1604, 1657, 2215, 2855, 2925, 3440 cm\(^{-1}\). HRMS (ESI, m/z): calculated for \( \text{C}_{32}\text{H}_{22}\text{FN}_{2}\text{O}_{2} \) [M + H]\(^+\): 485.1660, found: 485.1661.

9. Experimental procedures for synthesis of compound 7aa

A mixture of chiral catalyst (0.02 mmol, 0.2 equiv.), \( 1a \) (0.10 mmol, 1.0 equiv.) and \( 2a \) (0.10 mmol, 1.0 equiv.) and \( \text{CH}_2\text{Cl}_2 \) (1.0 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred
at 25 °C for the 24-120 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 3:1-2:1) to afford pure products 7aa. Yellow solid. ee as determined by HPLC (Chiralpak IC-H, 99:1 n-hexane/i-PrOH, 1.0 mL/min), tr (major) = 5.760 min, tr (minor) = 6.653 min. The ratio of 7aa-A/7aa-B was 0.51:1 as determined by 1H NMR. 1H NMR (500 MHz, CDCl3, a mixture of two isomers) δ 8.48 (d, J = 8.2 Hz, 1H, isomer A), 7.97 (d, J = 8.3 Hz, 1H, isomer B), 7.57 (t, J = 7.5 Hz, 1H, isomer A), 7.50 – 7.45 (m, 2H, isomer B), 7.44 (d, J = 7.8 Hz, 1H, isomer A), 7.39 (d, J = 7.6 Hz, 1H, isomer A), 7.30 – 7.21 (m, 4H, for isomer A and isomer B, overlapped), 7.21 – 7.15 (m, 3H, for isomer A and isomer B, overlapped), 7.04 – 6.96 (m, 3H, for isomer A and isomer B, overlapped), 6.96 – 6.81 (m, 4.5H, for isomer A and isomer B, overlapped), 6.75 (d, J = 2.3 Hz, 1H, isomer A), 6.64 (s, 1H, isomer B), 6.47 (d, J = 2.2 Hz, 1H, isomer A), 6.19 (s, 1H, isomer B), 6.00 (s, 1H, isomer A), 5.26 (s, 1H, isomer B), 5.21 (S, 1H, isomer A), 4.87 (s, 1H, isomer B), 3.94 (d, J = 17.9 Hz, 1H, isomer A), 3.70 (s, 1H, isomer A), 3.66 (s, 1H, isomer B), 3.62 (d, J = 18.8 Hz, 1H, isomer B), 3.17 (d, J = 18.7 Hz, 1H, isomer B), 2.99 (d, J = 18.0 Hz, 1H, isomer A), 1.40 (s, 9H, isomer A), 1.32 – 0.95 (m, 23H, for isomer A and isomer B, overlapped) ppm. 13C NMR (125 MHz, CDCl3, a mixture of two isomers) δ 181.1, 175.0, 154.9, 154.6, 153.9, 153.1, 151.4, 148.5, 136.9, 136.2, 136.1, 135.0, 134.8, 134.7, 131.6, 130.4, 129.6, 129.01, 128.9, 128.8, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 127.5, 127.3, 127.0, 126.7, 126.1, 125.4, 124.8, 123.8, 123.7, 121.5, 121.2, 117.0, 116.8, 115.0, 113.8, 113.7, 112.3, 79.9, 79.9, 75.8, 75.2, 59.1, 58.8, 56.2, 52.6, 43.5, 41.2, 34.4, 34.2, 34.1, 30.2, 30.1, 30.0.

**HPLC chromatogram of compound 7aa** (Chiralpak IC-H, 99:1 n-hexane/i-PrOH, 1.0 mL/min):

**Racemic:**
Enantioselective (A as a catalyst):

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<th>Relative Area (%)</th>
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Enantioselective (B as a catalyst):

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10. X-ray crystal structure of compound 3ar
Preparation of the single crystals of 3ar: pure compound 3ar (30 mg) was completely dissolved in the solvents of petroleum ether and DCM (20 mL, v/v = 1:2) at 2-8 °C. The bottle was sealed by a parafilm with several tiny holes, allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed on the wall and at the bottom of the bottle. Then, the crystals were chosen and subjected to the crystal X-ray diffraction analysis for the determination of the structure of 3ar. The crystal was kept at 296 K during data collection.

The relative configuration of product 3ar was determined by X-ray diffraction on Bruker D8 VENTURE PHOTON II diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 284(2) K using SAINT and SMART programs. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2270813). Crystallographic data and structure refinements for compound 3ar are listed in Table S2.

![Figure S1](image)

**Figure S1.** View of a molecule of compound 3ar with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.

**Table S3.** Crystal data and structure refinement for compound 3ar.

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<td>b/Å</td>
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\(\alpha/^{\circ}\) 90
\(\beta/^{\circ}\) 110.730(16)
\(\gamma/^{\circ}\) 90
Volume/Å\(^3\) 3322(3)
\(Z\) 1
\(\rho_{\text{calc}}\) g/cm\(^3\) 1.226
\(\mu/\text{mm}^{-1}\) 0.152
\(F(000)\) 1296.0
Crystal size/mm\(^3\) 0.16 \times 0.13 \times 0.07
Radiation MoK\(\alpha\) (\(\lambda = 0.71073\))
2\(\Theta\) range for data collection/° 4.122 to 56.928
Index ranges \(-12 \leq h \leq 12, -39 \leq k \leq 34, -13 \leq l \leq 13\)
Reflections collected 26901
Independent reflections 6529 [\(R_{\text{int}} = 0.2271, R_{\sigma} = \ldots\)]
Data/restraints/parameters 6529/0/414
Goodness-of-fit on \(F^2\) 1.015
Final R indexes [\(I \geq 2\sigma (I)\)] \(R_1 = 0.0863, wR_2 = 0.1941\)
Final R indexes [all data] \(R_1 = 0.2231, wR_2 = 0.2777\)
Largest diff. peak/hole / e Å\(^3\) 1.08/-0.38

11. X-ray crystal structure of compound 3ab’

Preparation of the single crystals of 3ab’: pure compound 3ab’ (15 mg) was completely dissolved in the solvents of petroleum ether and DCM (15 mL, v/v = 1:2) at room temperature. The bottle was sealed by a parafilm with several tiny holes, allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed on the wall and at the bottom of the bottle. Then, the crystals were chosen and subjected to the crystal X-ray diffraction analysis for the determination of the structure of 3ab’. The crystal was kept at 100 K during data collection.

The relative configuration of product 3ab’ was determined by X-ray diffraction on a Bruker APEX DUO system. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2268414). Crystallographic data and structure refinements for compound 3ab’ are listed in Table S3.
Figure S2. View of a molecule of 3ab’ with the atom-labelling scheme.
Displacement ellipsoids are drawn at the 30% probability level.

Table S4. Crystal data and structure refinement for 3ab’.

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<td>Wavelength</td>
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</tr>
<tr>
<td></td>
<td>b = 12.1164(2) Å, β = 90.4010(10)°.</td>
</tr>
<tr>
<td></td>
<td>c = 12.8017(3) Å, γ = 108.7490(10)°.</td>
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<tr>
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<tr>
<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>640</td>
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<tr>
<td>Crystal size</td>
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<tr>
<td>Index ranges</td>
<td>-11 &lt;= h &lt;= 13, -14 &lt;= k &lt;= 14, -15 &lt;= l &lt;= 15</td>
</tr>
<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 70.18°</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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Max. and min. transmission 0.96 and 0.74
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 6084 / 0 / 422
Goodness-of-fit on $F^2$ 1.056
Final R indices [I>2sigma(I)] $R1 = 0.0414$, $wR2 = 0.1120$
R indices (all data) $R1 = 0.0469$, $wR2 = 0.1157$
Largest diff. peak and hole 0.357 and -0.337 e.Å$^{-3}$

### 12. X-ray crystal structure of compound 5aa

Preparation of the single crystals of 5aa: pure compound 5aa (10 mg) was completely dissolved in the solvents of petroleum ether and DCM (20 mL, v/v = 1:3) at room temperature. The bottle was sealed by a parafilm with several tiny holes, allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed on the wall and at the bottom of the bottle. Then, the crystals were chosen and subjected to the crystal X-ray diffraction analysis for the determination of the structure of 5aa. The crystal was kept at 150.01 K during data collection.

The relative configuration of product 5aa was determined by X-ray diffraction on a Bruker D8 VENTURE PHOTON II diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) at 284(2) K using SAINT and SMART programs. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2268375). Crystallographic data and structure refinements for compound 5aa are listed in Table S4.

*Figure S3.* View of a molecule of 5aa with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
Table S5. Crystal data and structure refinement for 5aa.

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<td>Crystal size/mm³</td>
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<tr>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indexes [I&gt;=2σ (I)]</td>
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<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole / e Å⁻³</td>
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</table>
13. NMR spectra

$^1$H NMR spectra for compound 3aa (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3aa (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ab (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ab (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ac (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ac (100 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ad (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ad (100 Hz, CDCl$_3$)
$^{1}$H NMR spectra for compound 3ae (400 Hz, CDCl$_3$)

![NMR spectrum and structure of compound 3ae]
$^{13}$C NMR spectra for compound 3ae (100 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3af (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3af (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ag (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ag (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ah (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ah (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ai (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ai (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3aj (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3aj (125 Hz, CDCl$_3$)

| f1 (ppm) | 50.01 | 57.29 | 63.57 | 73.01 | 77.26 | 78.01 | 80.01 | 111.44 | 113.84 | 117.02 | 117.98 | 121.96 | 124.41 | 126.30 | 126.33 | 127.19 | 128.56 | 128.95 | 128.99 | 129.04 | 129.78 | 130.61 | 131.56 | 131.88 | 133.14 | 134.85 | 135.05 | 136.14 | 136.49 | 137.94 | 148.06 | 154.09 | 155.21 | 175.09 |
|---------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
$^1$H NMR spectra for compound 3ak (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ak (125 Hz, CDCl$_3$)
\[ ^1H \text{ NMR spectra for compound } 3\text{al (500 Hz, CDCl}_3\text{)} \]
$^{13}$C NMR spectra for compound 3al (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3am (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3am (100 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3an (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3an (125 Hz, CDCl$_3$)
**1^H NMR spectra for compound 3ao (500 Hz, CDCl₃)**

![NMR Spectrum Image]
$^{13}$C NMR spectra for compound 3ao (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ap (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ap (125 Hz, CDCl$_3$)

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F1 (ppm)
$^1$H NMR spectra for compound 3aq (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3aq (125 Hz, CDCl$_3$)
$^{1}$H NMR spectra for compound 3ar (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ar (125 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3as (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3at (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3at (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3au (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3au (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3av (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3av (125 Hz, CDCl$_3$)
\(^1\)H NMR spectra for compound 3aw (400 Hz, CDCl\(_3\))
$^{13}$C NMR spectra for compound 3aw (100 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ax (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ay (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ay (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3az (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3az (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3aa' (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3aa' (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ab' (500 Hz, CDCl$_3$)
\[^{13}\text{C} \text{NMR spectra for compound 3ab'} (125 \text{ Hz, CDCl}_3)\]
$^1$H NMR spectra for compound 3ac' (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ac' (100 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ad' (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ad' (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ae$'$ (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ae' (100 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3af' (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3af' (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ag' (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ag' (100 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ah' (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ah (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound $3\text{ba}$ (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ba (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ca (500 Hz, CDCl$_3$)
$^1$C NMR spectra for compound 3ca (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3da (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3da (125 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 3ea (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 3ea (125 Hz, CDCl$_3$)

$^1$H NMR spectra for compound 5aa (500 Hz, CDCl$_3$)
140
$^{13}$C NMR spectra for compound 5aa (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5aa (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ab (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ab (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound **5ab** (471 Hz, CDCl$_3$)

---

145
$^1$H NMR spectra for compound 5ac (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ac (125 Hz, CDCl$_3$)

![C NMR spectra graph]

Chemical shifts (ppm):

- 21.45
- 25.78
- 29.83
- 35.52
- 46.78
- 63.01
- 63.25
- 63.48
- 63.72
- 73.83
- 76.02
- 76.91
- 77.16
- 77.41
- 78.39
- 107.67
- 113.42
- 115.03
- 123.81
- 124.88
- 126.07
- 126.66
- 128.42
- 129.10
- 129.83
- 129.87
- 130.36
- 130.63
- 133.91
- 135.92
- 136.24
- 137.79
- 141.28
- 145.25
- 172.07
- 176.25
$^{19}\text{F}$ NMR spectra for compound 5ac (376 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ad (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ad (125 Hz, CDCl$_3$)
$^{19}F$ NMR spectra for compound 5ad (471 Hz, CDCl$_3$)
$^{1}$H NMR spectra for compound 5ae (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ae (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ae (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5af (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5af (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5af (500 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ag (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ag (100 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ag (376 Hz, CDCl$_3$)
$^{1}$H NMR spectra for compound 5ah (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ah (125 Hz, CDCl$_3$)

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Diagram of the $^{13}$C NMR spectrum.
$^{19}$F NMR spectra for compound 5ah (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ai (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ai (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ai (471 Hz, CDCl$_3$)

-74.24 ppm
$^{1}$H NMR spectra for compound 5aj (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5aj (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5aj (376 Hz, CDCl$_3$)

-74.13 ppm
$^1$H NMR spectra for compound 5ak (500 Hz, CDCl$_3$)
$^{13}\text{C}$ NMR spectra for compound 5ak (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ak (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5al (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5al (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5al (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5am (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5am (100 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5am (376 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5an (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5an (100 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5an (376 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ao (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ao (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ao (471 Hz, CDCl$_3$)

$\delta$ (ppm)
$^1$H NMR spectra for compound 5ap (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ap (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ap (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5aq (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5aq (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5aq (471 Hz, CDCl$_3$)
\(^1\)H NMR spectra for compound 5ar (400 Hz, CDCl\(_3\))
\(^{13}\)C NMR spectra for compound 5ar (125 Hz, CDCl\(_3\))
${}^{19}$F NMR spectra for compound **5ar** (471 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5as (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5as (100 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5as (376 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ba (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ba (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ar (376 Hz, CDCl$_3$)

\[ f_1 \text{ (ppm)} \]
$^1$H NMR spectra for compound 5ca (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ca (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ca (376 Hz, CDCl$_3$)

$\delta$ (ppm)
\(^{1}\text{H NMR spectra for compound 5da (500 Hz, CDCl}_3\)\)
$^{13}$C NMR spectra for compound 5da (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5da (376 Hz, CDCl$_3$)

$\delta$ (ppm) -74.29
$^1$H NMR spectra for compound 5ea (400 Hz, CDCl$_3$)

![NMR spectrum of compound 5ea]
$^{13}$C NMR spectra for compound 5ea (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ea (376 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5fa (400 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5fa (100 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5fa (376 Hz, CDCl$_3$)
$^1$H NMR spectra for compound 5ga (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 5ga (125 Hz, CDCl$_3$)
$^{19}$F NMR spectra for compound 5ga (376 Hz, CDCl$_3$)

$^1$H NMR spectra for compound 6 (500 Hz, DMSO-$d_6$)
$^{13}$C NMR spectra for compound 6 (125 Hz, DMSO-$d_6$)
$^1$H NMR spectra for compound 7aa (500 Hz, CDCl$_3$)
$^{13}$C NMR spectra for compound 7aa (125 Hz, CDCl$_3$)